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NGUYEN DUY THANH

RESEARCH ON MICROPLASTICS AND SOME RELATED COMPOUNDS ACCUMULATED IN GREEN MUSSELS IN THE COASTAL AREA OF QUANG NINH

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Supervisors:
1. Supervisor 1: Assoc.Prof.Phd. Do Van Manh, Institute of Science and Technology for Energy and Environment - Vietnam Academy of Science and Technology.
2. Supervisor 2: Prof.Phd. Trinh Van Tuyen, Institute of Science and Technology for Energy and Environment - Vietnam Academy of Science and Technology

Reviewer 1: Assoc.Prof.Phd. Van Huu Tap
Reviewer 2: Assoc.Prof.Phd. Bui Thi Kim Anh
Reviewer 3: Prof.Phd. Nguyen Manh Khai

The dissertation be examined by Examination Board of Graduate University of Science and Technology, Vietnam Academy of Science and Technology at 9 hour 00', date 06 month12 year 2024

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INTRODUCTION

1. The urgency of the thesis

Microplastics (MPs) are plastic particles ranging in size from 1 to 5000 μm and are similar in size to zooplankton or juvenile fish and can sink, settle in mud or sediment, or be suspended in seawater depending on the density of the polymer, age, and degree of environmental fouling. Therefore, marine organisms such as zooplankton, bivalves, and fish that accidentally ingest MPs will be stored in cells or tissues. In addition, additives such as BPA, PAEs, and PBDEs have been detected in various environments such as water, sediments, and living organisms, and their presence is closely related to the level of MPs contamination. Upon degradation, additives such as BPA, PAEs, and PBDEs can leach from microplastic waste, posing a significant environmental and ecological threat to the receiving watershed. On the other hand, additives have the potential to affect humans through the food chain and biomagnification.

The presence of MPs in coastal areas, especially accumulation in marine species of Vietnam, has also been observed in several recent studies. Although there are research reports collected from several different species in marine areas, there has been no study published in Vietnam on accumulation in green mussels *(Perna viridis)*. In addition, green mussels are bivalves that are widely used as food in Vietnam in general, and in Quang Ninh province in particular. Therefore, it is necessary to research the ability to accumulate MPs and some chemicals such as BPA, PAEs, and PBDEs in green mussels. The research results presented in this thesis will be the scientific basis for assessing the accumulation of some chemicals (BPA, PAEs, and PBDEs) with microplastics between chemicals and MPs in sediment

samples and green mussels at some coastal locations in Quang Ninh province.

2. Research objectives of the thesis

- The study determined the density, size, and composition of MPs accumulated in green mussels *(Perna viridis)*, seawater, and sediments. In addition, the study also determined the concentrations of some chemicals (BPA, PAEs, and PBDEs) related to MPs.

- The study determined the accumulation index and risk index of MPs and organic substances based on the chemical toxicity indexes of polymers, PLI load, and bioaccumulation - sediments, and evaluated the correlation between MPs and some organic substances BPA, PAEs, and PBDEs.

3. New point of the thesis

- The quantity, shape, size, and composition of MPs, and some typical organic substances accumulated in green mussels, seawater, and marine sediments in the coastal waters of Quang Ninh province have been quantified.

- The correlation between MPs and some related organic substances and the accumulation level, risks of MPs, and accompanying chemicals based on chemical toxicity indexes of polymers, PLI load, and bioaccumulation - sediments has been determined.

- Initially, it can be determined that Green Mussels are one of the bivalve species suitable as biological indicators for assessing the exposure status of MPs and related chemicals (introduced in the production process of plasticizers, shapers, slow-burning, colorfast substances...) in the coastal marine environment of Vietnam.

CHAPTER 1. OVERVIEW OF RESEARCH ISSUES

Chapter 1 consists of 28 pages, stating the urgency of the thesis research direction such as research in the field of MPs and chemicals related to plastic production that accumulate in bivalves, especially green mussels, the object used as human food in Vietnam is still new and very few studies have mentioned it. Furthermore, this research aims to be carried out on a large spatial scale and stretches across the entire coastal region of Quang Ninh.

The overview section also summarizes research on MPs pollution and associated chemicals accumulating in seawater, sediment, and bivalve environments around the world as well as in Vietnam have evaluated the shortcomings, difficulties, and comments and then proposed issues that need to be resolved in this thesis.

In addition, the risk of MPs and chemicals accumulating in bivalves is also specifically addressed. Most chemicals used to produce plastic polymers have the risk of causing damage to the environment and ecosystem when released during production and the use and disposal of plastic products leads to a potential risk of MPs which is their ability to accumulate in the bodies of marine organisms. Bivalves (oysters, oysters, clams, and green mussels) are useful for assessing the bioaccumulation of MPs due to their important role in ecosystem function.

The specific characteristics of the natural and socio-economic conditions in the research area have also been indicated, with specific assessments and comments associated with the research contents that the thesis needs to address.

From the above comments, the research PhD has come up with research objectives and content that are appropriate to actual conditions and linked to the issues identified in the literature review.

CHAPTER 2. RESEARCH SUBJECTS AND METHODS

Chapter 2 includes 26 pages, detailing the selection of research objects in the thesis, which are green mussels, seawater, and sediment in the coastal area of Quang Ninh (Figure 2.1), and the MPs analysis procedure used in this study was based on Teng's method. J et al., and Munno et al., after being adjusted and set up to suit laboratory conditions and using μ-FTIR analysis technique in ATR reflection mode to analyze MPs.

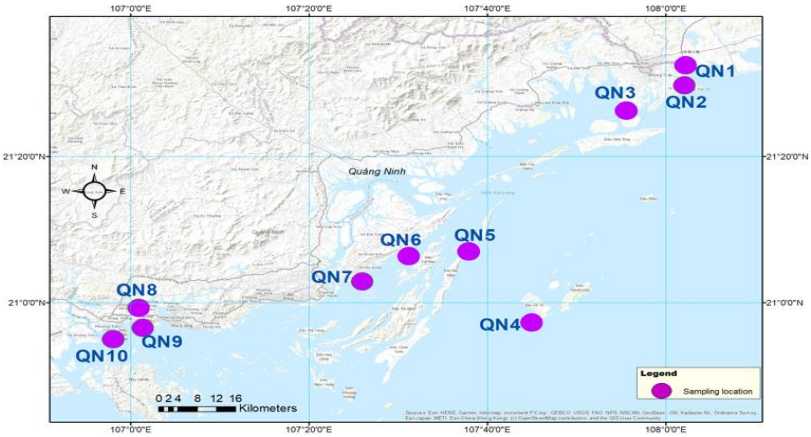

Figure 2.1. Location of research samples

This chapter also details the method of analyzing chemical components (BPA, PAEs, and BPDEs) accumulated in green mussels and sediments. The procedure is referred to standard extraction method in the US.EPA Method 3540C and cleaning standard US.EPA Method 3630C.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Characteristics of microplastics accumulating in green mussels, seawater, and sediments

3.1.1. Determination of microplastic density

MPs density in green mussel samples at 10 research locations ranged from 4 to 78 MPs/individual, with an average value of 22.26 ± 16.05 MPs/individual. Regarding tissue weight, MPs density also fluctuated greatly from 0.37 to 18.24 MPs/g w.w, with an average value of 3.41 ± 2.97 MPs/g w.w. Notably, the highest MPs density was recorded at location QN4 (34.75 ± 28.03 MPs/individual and 5.43 ± 4.21 MPs/g w.w), which is a sampling location in the famous tourist beach area of Co To island. Meanwhile, the lowest MPs density was recorded in individual and soft tissue samples collected at QN3 (14.38 ± 5.60 MPs/individual) and QN7 (1.10 ± 0.53 MPs/g).

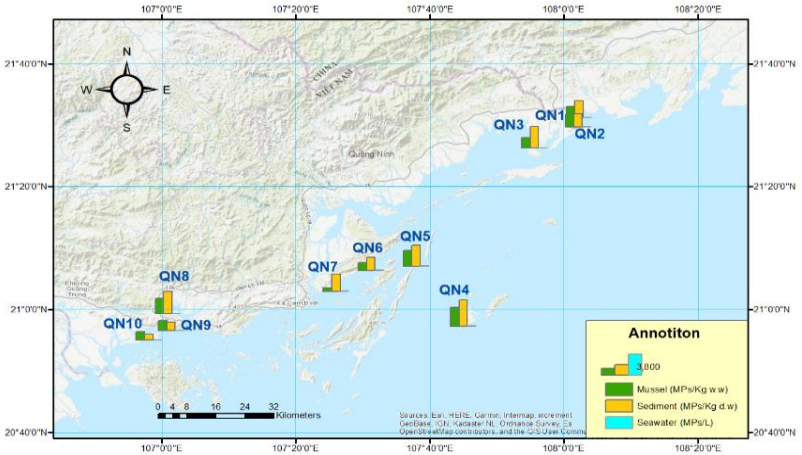

Figure 3.1. Density of MPs accumulates in green mussels, seawater and sediments in the coastal area of Quang Ninh

The results of MPs analysis in seawater samples ranged from 43.33 to 146.67 MPs/L, QN7 (146.67 ± 4.41 MPs/L) had the highest MPs density in surface seawater while QN3 (43.33 ± 3.34 MPs/L) had the lowest MPs density in surface seawater. The results of MPs analysis in sediment samples at 10 locations had MPs density ranging

from 1700 to 7600 MPs/kg d.w. The sediment sample collected at point QN4 had the highest MPs density (7600.00 ± 655.74 MPs/kg) in the tourist beach area of Co To island. This value correctly reflects the correlation (Figure 3.1).

Pearson correlation and linear correlation calculations showed that there was no low correlation or negative correlation between MPs density in water and sediment ($r = -0.3227$, $p > 0.05$; $a = -0.0056$, $R^2 = 0.1041$) as well as between blue mussels and water ($r = -0.3350$, $p > 0.05$; $a = -13.163$, $R^2 = 0.1122$) while a moderate correlation was observed between MPs density in sediment and blue mussels ($r = 0.4825$, $p > 0.05$; $a = 0.3297$, $R^2 = 0.2328$).

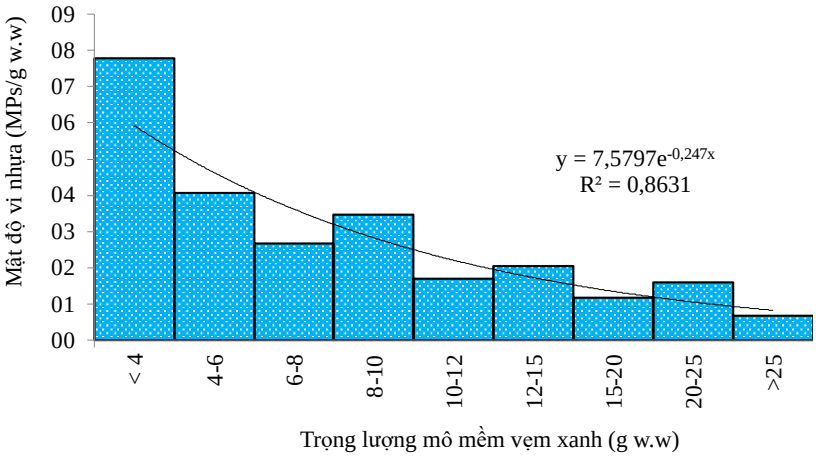

Figure 3.2. Distribution of MPs according to soft tissue weight of mussels

For the green mussel sample, at 10 sampling locations, the length, width, and soft tissue weight of the green mussel were respectively: 4.80 - 13.50 cm (Average: 8.48 ± 1.56 cm); 2.60 -5.90 cm (Average: 3.81 ± 0.66 cm) and 2.37 - 35.56 g w.w (Average: 8.45 ± 6.14 g w.w) shown in Figure 3.2. The results of one-way variance calculations showed that

there was no difference in MPs density in green mussels at sampling locations, according to soft tissue weight ($p = 0.1395$) and by individual ($p = 0.3920$). Similarly, the correlation results between mussel meat density and mass had no relationship with $r = -0.3631$. This means that a negative correlation trend was identified between mussel meat mass and MPs density with coefficient $a = -0.247$ and $R^2 = 0.8675$ (Figure 3.2).

In addition to the research results on MPs accumulation in green mussels, seawater, and sediments, some research results during the thesis implementation process that the PhD student participated in with the group of authors Manh et al., on assessing the presence of MPs in oysters, seawater and sediments in coastal areas across Vietnam showed that the density of MPs accumulated in Pacific oysters *(Crassostrea gigas)* in Da Nang Bay, Vietnam was on average 1.88 ± 1.58 MPs/g w.w and 18.54 ± 10.08 MPs/individual and the research results on oysters in 16 coastal provinces in Vietnam including Quang Ninh showed that the average MPs was 1.18 ± 0.59 MP/g w.w or 11.55 ± 4.83 MPs/individual. MPs in beach sand near a refinery on the central coast of Vietnam at 11 sampling sites showed that MPs were present in all collected samples with an average density of 1582 ± 660 MPs/kg. Similarly, MPs accumulation in sediments at 3 beaches in Da Nang, My Khe, T20, and Son Thuy, with average MPs densities at the 3 beaches Son Thuy, T20, and My Khe being 1,460 ± 758, 1,799 ± 370, and 29,232 ± 2,577 pieces/kg d.w., respectively. At Le Thuy Beach, Quang Ngai province, MPs accumulated in surface seawater samples had MPs density ranging from 19.44 ± 7.12 to 50.56 ± 2.51 MPs/L, with an average of 38.09 ± 10.84 MPs/L. In beach sand samples, MPs density ranged from 783.33 ± 75.28 to 1,950.00 ±

104.88 MPs/kg with an average value of 1,283.33 ± 378.32 MPs/kg.

3.1.2. Determine the shape and size of microplastics

Research results show that MPs found in mussels and seawater and sediment environments have the main shapes of pieces, fibers, and particles as specifically shown in Figure 3.3.

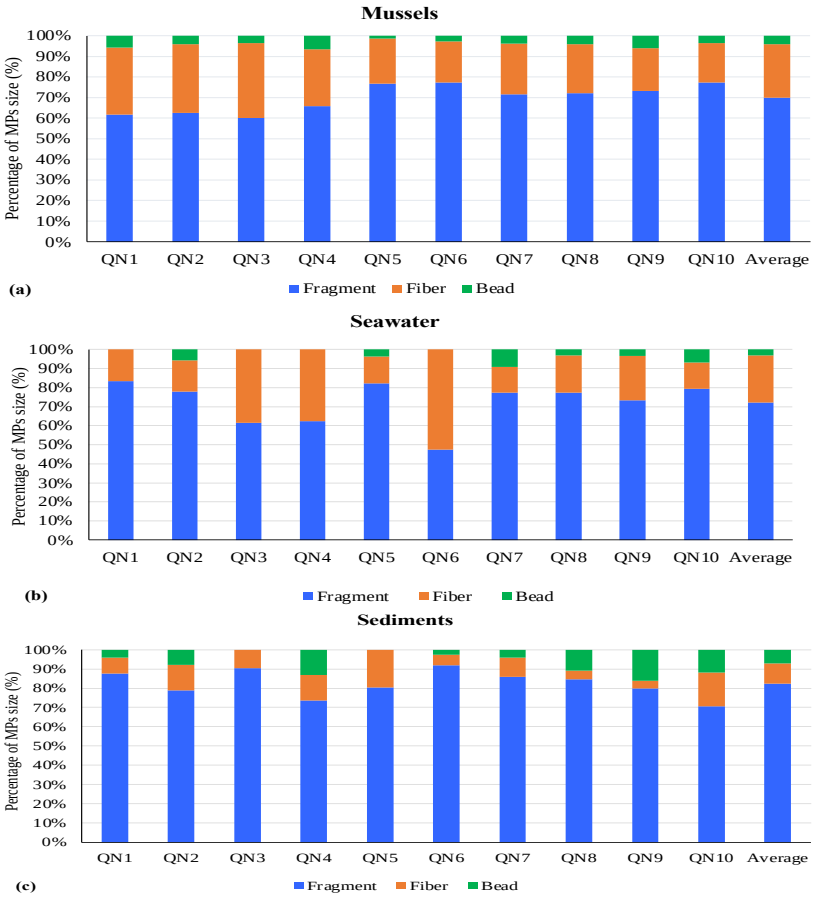

Figure 3.3. Distribution of MPs shapes in the research in mussels (a), seawater (b), and sediments (c)

The results of the study showed that the average size of MPs in

mussel samples was 119.72 ± 171.93 µm, ranging from 19.40 - 2377.8 µm, MPs in seawater samples ranged from 22.5 to 795.1 µm and averaged 116.99 ± 110.76 µm. Meanwhile, in sediment samples, MPs ranged from 22.3 to 1032.3 µm and averaged 97.61 ± 89.74 µm.

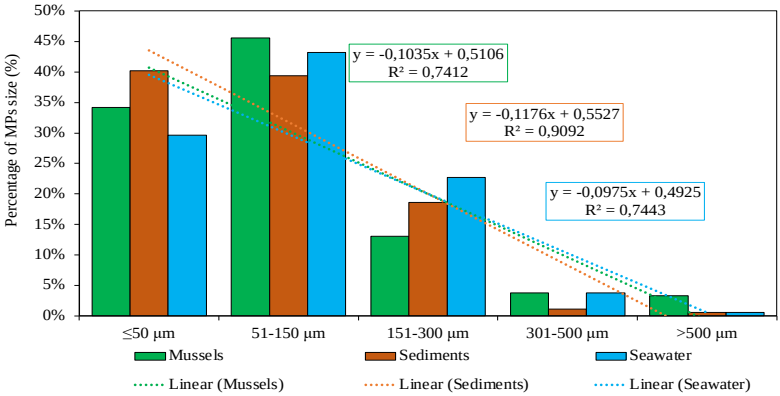

Figure 3.4. Size distribution of MPs in mussels, seawater, and sediments

MPs in the size groups 0 - 50 µm and 51 - 150 µm were dominant in both green mussels and the environment, with distribution ratios of 34.17% and 45.62% in mussel samples; 29.65% and 43.20% in seawater samples and 40.22% and 39.40% in coastal sediment samples, respectively. In general, MPs density tended to be higher at small sizes (<150 µm) in both mussel, seawater, and sediment samples with linear coefficients R^2 of 0.7412; 0.9092, and 0.7443 (Figure 3.4).

When the research results of MPs accumulated in green mussels, seawater, and sediments of the thesis were compared with the research results of the same group of authors Manh et al., it was shown that the shape and size of MPs in Pacific oysters *(Crassostrea gigas)* in Da Nang Bay had 3 main forms: fragments, fibers, and particles corresponding to 73.71; 25.84 and 0.45% respectively, the size of MPs ranged from 22.4 - 1,318.8 µm, the most common being the size under

100 μm, accounting for 77.30%. Similarly, the results of oyster research in 16 coastal provinces across Vietnam including Quang Ninh showed that MPs were in the form of fragments (62.40%), fibers (37.10%), and particles (0.50%) and the size of all MPs in oyster samples varied from 20 - 998 μm, with an average of 112.04 ± 124.72 μm and the results of shape and size of MPs in the beach sand near an oil refinery on the central coast of Vietnam at 11 sampling locations showed that fibers accounted for the largest proportion in the samples with 57.11%, the rest were classified as fragments. The average size of MPs was 83.1 ± 74.3 μm, the size of MPs in sediments at 3 beaches in Da Nang, My Khe, T20, and Son Thuy, ranged from 22.7- 1,272.6 μm, with an average of 113.9 ± 152.8 μm, MPs with a size smaller than 150 μm accounted for the largest proportion: 77.83% in Son Thuy, 87.96% in T20 and 65.91% in My Khe. At Le Thuy beach, Quang Ngai province, the results of MPs in sea sand and surface water samples showed that the average MPs size was 150.90 ± 1,50.07 μm, ranging from 22.5 - 838.9 μm in seawater samples, in beach sand samples the MPs size ranged from 22.5 - 539.3 μm, averaging 84.68 ± 78.96 μm. MPs in the size groups 0 - 50 μm and 51 - 100 μm accounted for the majority in all samples with distribution ratios of 28.75 and 23.75% in seawater samples; and 41.56 and 31.82% in beach sand samples, respectively. Fragments were predominant in both seawater and sand samples, accounting for 57.50% and 92.86%, respectively.

3.1.3. Determine the chemical composition (polymer) of microplastics

The results of the MP evaluation were analyzed using a Nicolet iN10MX infrared microscope. 16 types of polymers of MPs have been identified in mussel bodies and 11 types of polymers of MPs in seawater and sediments in the study area in which PET accounts for

the highest proportion with 53.13% in mussels, followed by PA and PE accounting for 15.35% and 7.51% respectively.

Similarly, research results in the environment also show that PET contains the majority of polymers with 58.44% in seawater, and 49.93% in sediment, followed by PA and PTFE accounting for 12.62% and 10%. 75% in seawater, 8.59%, and 16.54% in sediment. All of this data is shown in Figure 3.5.

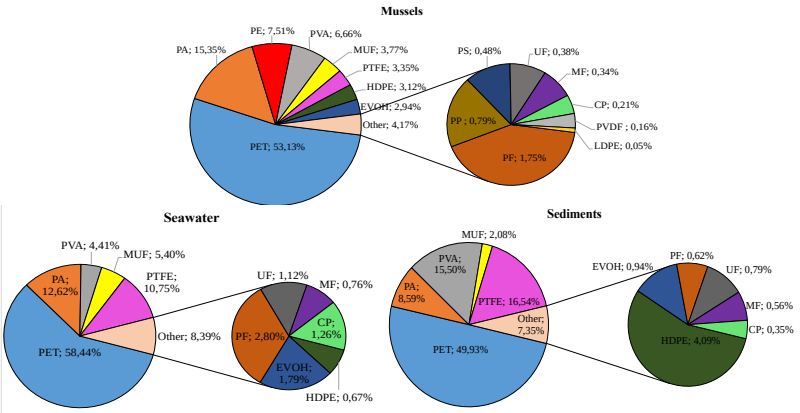

Figure 3.5. Polymer composition of MPs accumulated in green mussels, sediments and seawater

In addition to the research results in the coastal area of Quang Ninh, during the thesis implementation, the PhD student participated in the research with the group of authors Manh et al., on the chemical composition (polymer) of MPs in oysters, water, and sediments in coastal areas across Vietnam in the Da Nang and Quang Ngai seas, with the following results: The MPs composition accumulated in oysters *(Crassostrea gigas)* in Da Nang Bay has 15 types of polymers, of which nylon is the most abundant polymer with 50.56%. Similarly, the research results of oysters in 16 coastal provinces of Vietnam

(including the coastal area of Quang Ninh) have 12 types of MP polymers identified, of which PET and HDPE are identified as the main polymer components of MPs, accounting for 42.26% and 31.95% of the total MPs, respectively. The MPs composition accumulated in sand and surface water at Le Thuy beach, Quang Ngai province with the main polymer type being PET with the proportions of 37.50 and 44.16% respectively in seawater and sand samples and in sediments at 3 beaches in Da Nang, My Khe, T20 and Son Thuy. The chemical composition of MPs with different polymer types was determined with 3 polymer types PTFE, EVOH, and PA accounting for a high proportion of the samples.

3.2. Determine the cumulative index and risk index of microplastics

3.2.1. Determination of microplastic accumulation index in green mussels

Research results show that the bioaccumulation index (BCR) and bioaccumulation index - sedimentation index (BSAF) show that there is a relatively high accumulation of MPs in the mussel body, specifically the BCR value and BSAF is 1.05 and 10.38, respectively. High BSAF values indicate high absorption and accumulation of MPs from green mussel organs. The study shows that green mussel biomarkers have the potential to be used as sensitive, accurate, and rapid techniques to assess the biological effects of environmental pollutants in coastal waters. Thus, the results of this study show that green mussels can accumulate MPs (BCR>1 and BSAF>1).

3.2.2. Determine the risk index of microplastics

The results of calculating the ecological risk index from the polymer composition (H) of MPs and the pollution load index of MPs (PLI) at 10 green mussel sampling points are shown in Figure 3.6.

The MPs pollution load index in green mussels at 10 research

locations in the coastal area of Quan Ninh is quite high, with PLI ranging from 5.23 to 11.65. Among them, the location with the highest MPs pollution load index is QN4 with PLI = 11.56, followed by QN5 (10.64); QN8 (10.48), QN9 (10.05) these locations according to MPs pollution risk criteria are designated as level II, meaning they have quite high pollution levels. The remaining results at the location with a lower PLI index are designated as a level I, meaning there is a lighter MPs pollution level, including QN2 with PLI = 9.58, QN1 (8.95), QN3 (8.80), QN10 (7.89), QN6 (7.32) and the lowest value is position QN7 with PLI index = 5.23.

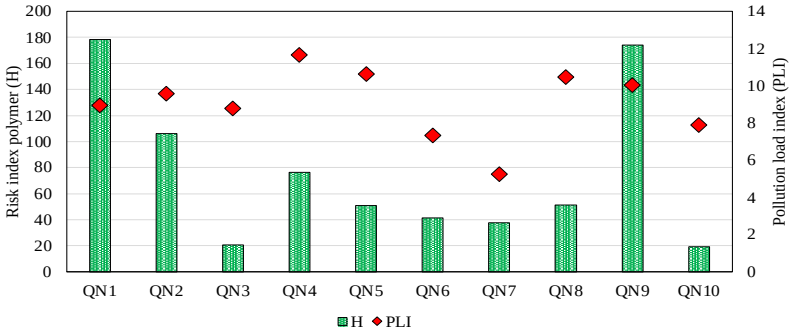

Figure 3.6. Polymer risk index and MPs pollution load index accumulated in green mussels

Research results showed that the H index accumulated in green mussels at 10 sampling locations ranged from 19.27 to 178.55 and the average was 75.67 ± 55.89. Specifically, the risk index of green mussels at points QN1 (178.55), QN2 (106.20), and QN9 (174.17) are at level III danger (100 - 1000) and the remaining points have an index at level II (100).

Specifically, the highest value in the sediment samples is at site QN4 with PLI = 7.03, followed by sites QN8(6.50), QN3(6.35);

QN5(6.29); QN7(5.70); QN1(5.64); QN2(4.97); QN6(4.90); QN9(4.03) and the smallest value is at point QN10 with PLI = 3.32 (Figure 3.7).

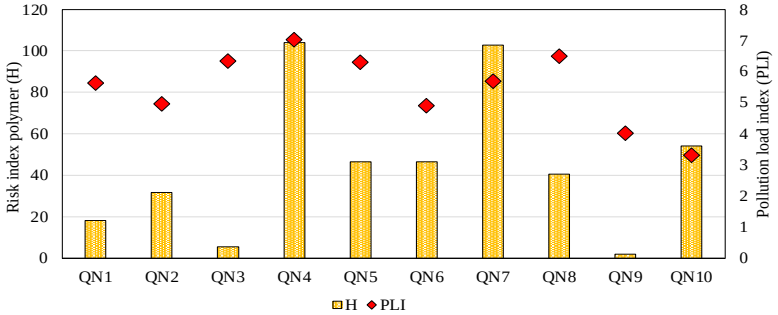

Figure 3.7. Polymer risk index and MPs pollution load index accumulated in sediments

These PLI values indicate that the concentration of MPs in the beach sediment sample is at hazard level I, i.e. mild pollution. One-way ANOVA calculation showed that PLI values were significantly different among the 10 sampling points with $p < 0.05$.

However, the MP's pollution load index in seawater samples is very high, with 9/10 locations at level IV with PLI values ranging from 32.66 to 54.16. Specifically, the MPs pollution load index at location QN7 has PLI = 54.16, followed by QN2(48.99), QN8(45.46), QN9(44.72), QN10(43.97), QN5(43.20), QN6(35.59) QN1(34.64) and QN4 have PLI = 32.66. One location giving MPs pollution load index results at level III is QN3 with PLI = 29.44 (Figure 3.8).

Research results show that the hazard index of polymer components at 10 seawater sampling locations has the H index at locations QN3 of 118.46, followed by QN4(116.38), QN5(140.21) QN6(100.68), QN7(220.54), QN9(162.00) and QN10(135.44) have exceeded the dangerous threshold level III, the remaining points have H index at level II. However, the H index in sediment is quite low,

ranging from 2.12 - 103.89, an average of 45.17 ± 33.48, and most have an H index at levels I and II, with two points being QN4(103.89) and QN7(102.80) at level III.

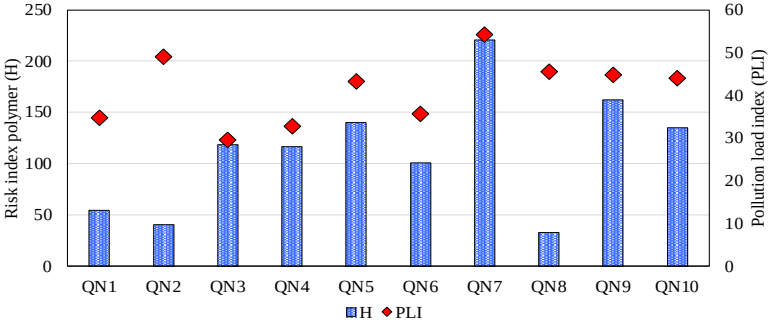

Figure 3.8. Polymer risk index and MPs pollution load index accumulated in seawater

3.3. Determine the concentration of BPA, PAEs, and PBDEs accumulated in green mussels and sediment

3.3.1. Determination of BPA concentration accumulated in green mussels and sediments

Research results showed that BPA concentration accumulated in green mussel samples at 10 coastal locations in Quang Ninh ranged from 29.13 - 1640.37 µg/kg ww with an average of 406.98 ± 492.02 µg/kg w.w and the highest BPA concentration in green mussels was found in the waters of Tra Co (QN2; 1,640.37 ± 42.67 µg/kg w.w), Van Ninh (QN3; 670.90 ± 21.86 µg /kg w.w) and Bai Chay (QN9; 675.30 ± 49.20 µg/kg w.w). In coastal sediment samples, BPA concentrations ranged from 0.03 - 1.79 µg/kg d.w with an average of 0.23 ± 1.79 µg/kg d.w and the locations with the highest BPA concentrations in sediment were QN3, QN4, and QN8. To simulate the BPA concentration value more clearly in the assessment of each

location, the research results are shown in Figure 3.9.

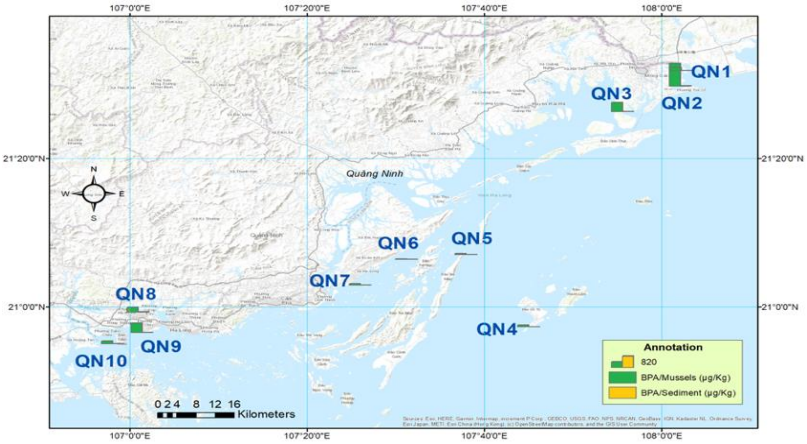

Figure 3.9. BPA concentration accumulated in green mussels and sediments in the coastal area of Quang Ninh

The results of correlation calculations showed that there was a correlation between BPA concentrations in green mussels and sediment samples (a = -0.0001, R^2 = 0.0087; r = -0.0931) across the study area.

3.3.2. Determine of PAEs concentration accumulated in green mussels and sediments

Research at 10 sampling locations showed that the concentration of $\sum_{13}$PAEs compounds detected in green mussel samples ranged from 35.74 - 1747.16 µg/kg w.w and with an average level of 523.93 ± 595, 29 µg/kg w.w. The concentration of $\sum_{13}$PAEs in sediment ranged from 47.16 - 295.48 µg/kg d.w, with an average of 144.32 ± 81.53 µg/kg d.w, specific concentrations at 10 locations are presented in Figure 3.10.

Green mussel samples showed that the location with the highest exposure to PAEs was in Ha Long waters, Van Don district (QN6) with a concentration of 1,747.16 ± 58.66 µg/kg w.w, followed by location

QN2 (1,277.05 ± 21.96 µg/kg w.w), QN9 (827.70 ± 86.60 µg/kg w.w), QN3 (661.98 ± 67.29 µg/kg w.w) and QN1 have a $\sum_{13}$PAEs concentration of 276.64 µg/kg w.w. However, PAEs accumulated in sediments with the highest concentration occurred in Cai Rong sea area, Van Don district (QN7) at 295.48 ± 22.48 µg/kg d.w and followed by locations QN10 at 232.82 ± 29.90 µg/kg d.w, QN9 (215.05 ± 53.80 µg/kg d.w), QN1 (162.05 ± 7.10 µg/kg d.w) and QN2 have a PAEs concentration value of 150.59 ± 15.47 µg/kg d.w. The results of correlation calculations showed that there was a low correlation between PAEs concentrations in green mussels and sediments (a = 14.751, R^2 = 0.3039; r = -0.1349) at the sampling locations.

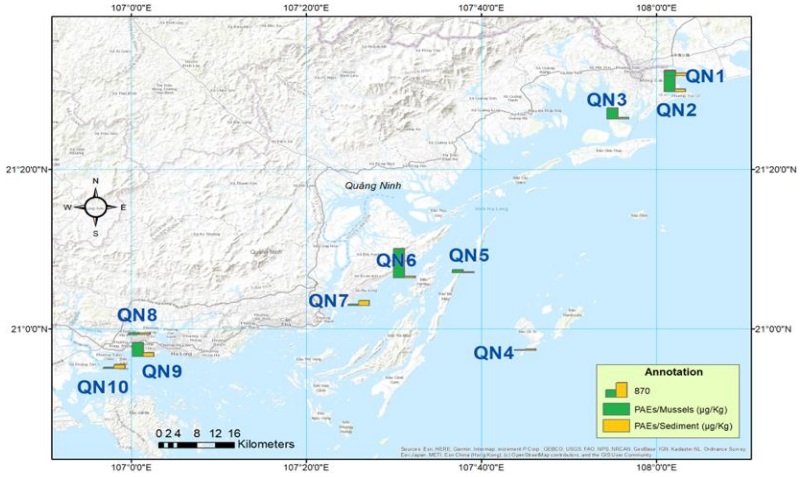

Figure 3.10. PAEs concentration accumulated in green mussels and sediments in the coastal area of Quang Ninh

The analytical results shown in Figure 3.11 show that five out of thirteen congeners of PAEs analyzed were detected with a frequency of 5 - 34% in green mussel samples and in sediments, eight out of thirteen congeners of PAEs were detected ranging from 5 to

28%. The substances that occupy the most amount of green mussels are BMPP (34%), DnHP (33%) and DEHP (10%), however, the substances that occupy the most in sediment are DnHP (28%), DMEP (21%).) and DEHP (12%). BEEP and DCP congeners were not found in any of the green mussel and sediment samples. This may be due to the characteristics of environmental conditions in the study area.

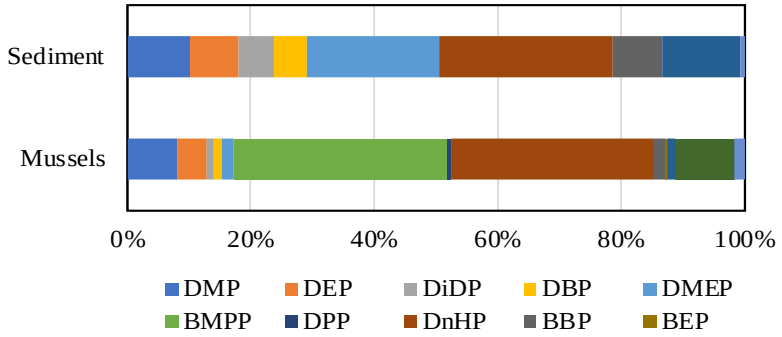

Figure 3.11. Ratio of PAEs content in sediment and green mussels.

The high concentrations of PAEs quantified in green mussels indicate the potential for bioaccumulation of these chemicals in the body of this species.

3.3.3. Determine the concentration of PBDEs concentration accumulated in green mussels and sediments

In this study, the value of $\sum_5$PBDEs was the sum of all PBDEs congeners. For all samples, $\sum_5$PBDEs concentrations in green mussels ranged from 0.06 - 23.50 µg/kg ww, with an average of 8.60 ± 9.44 µg/kg ww. Similarly, $\sum_5$PBDEs concentrations in sediments ranged from 0.06 - 7.26 µg/kg dw and averaged 1.99 ± 2.43 µg/kg dw, specific concentrations at 10 locations are presented in Figure 3.12.

The results show that the concentration of $\sum_5$PBDEs is quite high, at the research location in the Tra Co sea area (QN2 - 23.50 ± 4.76 µg/kg w.w) followed by location QN1 (19.34 ± 1.53 µg/kg w.w), QN5 (18.60 ± 2.29 µg/kg w.w) and position QN3 is 18.39 ± 1.88 µg/kg w.w, however at positions QN4, QN7, QN8 and QN10 has very low concentrations of $\sum_5$PBDEs. Through the cumulative levels of $\sum_5$PBDEs values obtained from the study, it shows that the waters of Tra Co (QN2), Hai Hoa (QN1) and Van Ninh (QN3) are located in the ocean current from the North and $\sum_5$PBDEs brought from the mainland through the flow into the Ka Long River, this is considered a cause of higher accumulation of PBDEs here than in the rest of the region. This level has a high correlation when considering the $\sum_5$PBDEs value in sediment samples.

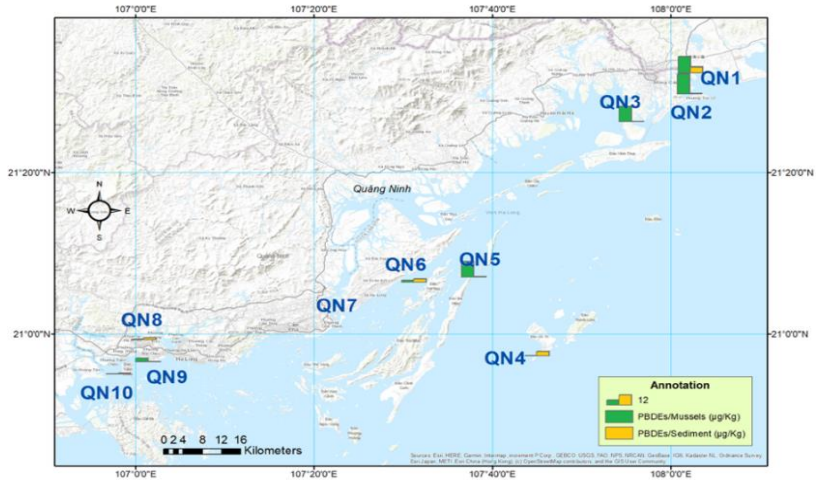

Figure 3.12. PBDEs concentration accumulated in green mussels and sediments in the coastal area of Quang Ninh

Meanwhile, the concentration of $\sum_5$PBDEs in sediments at locations in Hai Hoa waters (QN1; 7.26 ± 1.67 µg/kg d.w) was

recorded at the highest value, gradually decreasing values at position QN4 (4.87 ± 1.16 µg/kg d.w) and followed by QN6 (4.14 ± 1.90 µg/kg d.w). The results of linear correlation calculations showed a negative correlation between the concentrations of ∑5PBDEs in green mussels and sediments (a = -0.0102, R^2 = -0.0016; r = -0.1760) at the 10 study locations above.

Research results in Figure 3.13 show that BDE-47 concentration in green mussels is the highest, ranging from 0.06 - 18.50 µg/kg w.w with an average value of 28.13 ± 6.45 µg/kg w.w, followed by BDE-28 with concentrations from 0.06 - 8.93 µg/kg w.w with an average value of 5.15 ± 2.91 µg/kg w.w. However, in coastal sediments, BDE-183 concentration has the highest value with a value range of 0.06 - 7.02 µg/kg dw and an average value of 5.19 ± 1.83 µg/kg d.w, followed by BDE-47 concentrations ranging from 0.06 - 3.32 µg/kg d.w with a mean value of 1.02 ± 0.99 µg/kg d.w.

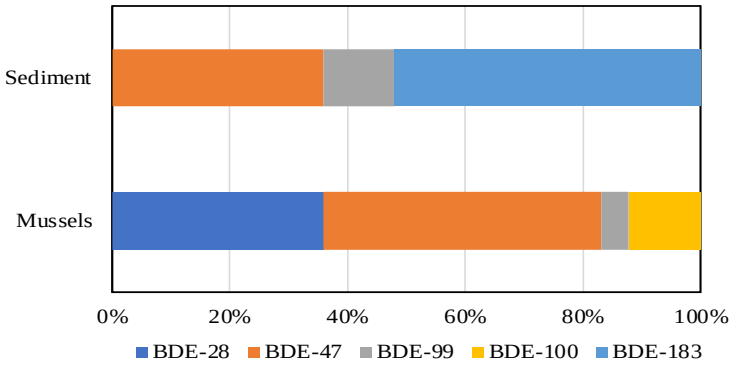

Figure 3.13. The ratio of PBDEs content in sediment and green mussels.

The most abundant congeners in green mussels are BDE-47 accounting for 46.55%, followed by BDE-28 with 35.35%, BDE-100

(12.32%), BDE-99 (5.10%) and BDE-183 (0.68%). The proportion of BDE-47 in both environments is about 33 - 47%. However, the relative concentrations of BDE-99 decreased in the order sediment > green mussels.

Research results show that the concentration of congeners accumulated in sediments is BDE-183, which has the highest value at 48.77%, followed by BDE-47 accounting for 33.00%, and BDE-99 (12.84%), BDE-100 (2.69%) and BDE-28 (2.69%). Among the five congeners, BDE-47 predominates in both sediment and green mussels, and BDE-183 predominates in sediment, whereas the ratio of BDE-183 in green mussels has shallow values (Figure 3.13).

The green mussel *(Perna viridis)* is a stationary species that clings to objects suspended in the water, while the remaining species live on the bottom. Therefore, the metabolism of mussels in the water environment is continuous, so they are one of the species that can be used as an indicator to assess environmental pollution due to the accumulation of BPA, PAEs, and PBDEs.

3.4. Determine the BSAF index and evaluate the correlation of MPs with related chemicals accumulated in green mussels

3.4.1. Determine the BSAF index

The bioaccumulation coefficient for each compound (BPA, PBDEs, and PAEs) in green mussel samples and sediments in the coastal area of Quang Ninh was determined and the BSAF results of BPA at 10 research locations were within the range from 108.03 to 584.47, the average value is 286.24 ± 198.95. However, among the 10 research locations, locations QN1, QN2, QN7, and QN9 have unknown values due to the very low concentration of BPA accumulated in sediment, the location with the highest value is QN8 (584,47), followed by QN10(407.85), QN3(374.89) and QN6(126.65). Similarly, the

BSAF value of ∑PAEs ranges from 0.22 to 17.94, with an average value is 4.57 ± 5.57, in which the position with the highest value is QN6(17.94), followed by QN2(8.48) and QN3(7.84), the lowest position is QN7(0.22). For the BSAF value of ∑PBDEs at 10 research locations, the value ranges from 0.55 to 63.41 and the average value is 28.89 ± 32.07, of which locations QN2, QN4, QN7, QN8, QN9 and QN10 have unknown values due to the concentration of PBDEs accumulated in green mussels and sediments below the detection threshold, the position with the highest value is QN3(63.41), followed by QN5(48.95) and QN1(2.66), the lowest position is QN6(0.55). The BSAF values of the above substances and compounds reflect the contribution of sediment to the bioaccumulation of the substances.

3.4.2. Evaluate the correlation of MPs with related chemicals accumulated in green mussels

The results of calculating the linear correlation between MPs with BPA, PBDEs and PAEs showed that there was a low statistical correlation between MPs density and BPA (a = 0,3758, R^2 = 0,0209; r = 0,14) and PBDEs (a = 18.996, R^2 = 0.0217; r = 0,37) concentrations accumulated in green mussels or determined a negative correlation trend between the accumulation of MPs and PAEs (a = -0.4643; R^2 = -0.0467; r = -0,22) in green mussels. Thus, the correlation between MPs and BPA and PBDEs accumulated in green mussels was not clear, highlighting the complex interactions between these pollutants.

The MPs concentration results obtained in this research for organisms, seawater, and sediments were higher than previously published studies in other regions of the world, which likely contributed to the causing BPA, PAEs, and PBDEs pollution in green

mussels and due to additives from microplastics being released into the environment. However, the negative correlation between MPs density and BPA and PAEs concentrations accumulated in green mussels highlights the complex interactions between these pollutants.

NOVEL CONTRIBUTIONS OF THE THESIS

Conclude:

1. The results show that the average density of MPs in mussels is quite high, on average 3.41 ± 2.97 MPs/g w.w and 22.26 ± 16.05 MPs/individual, and the density of MPs in the environment seawater and sediment were 88.00 ± 30.88 MPs/L and 4,800.00 ± 1,775.95 MPs/kg dw, respectively. The common shapes of MPs in the 3 research subjects were determined to be fragments, fibers, and particles. In addition, MP sizes from less than 50 µm and 51-150 µm are the most common. Sixteen polymers were identified that accumulate in green mussels. Eleven polymers have been identified in seawater and sediment environments.

The results of calculating this PLI value indicate that the concentration of MPs in the beach sediment sample is at hazard level I, a mild pollution level. However, the MPs pollution load index in seawater samples is very high, with 9/10 locations at level IV with PLI values ranging from 32.66 to 54.16. Based on the chemical composition of the polymer, the risk assessment index (H) is at levels II and III in green mussels, seawater, and sediments. The biological density index between green mussels and seawater at all locations showed high results (BCR > 1). Similarly, the sediment bioaccumulation coefficient at the study location has BSAF > 1, on average more than 10 times.

2. The results of BPA concentration in green mussels are quite high (varying from 29.13 to 1640.37 µg/kg ww) and in coastal sediment samples, BPA concentration ranges from 0.03 - 1 .79 µg/kg dw with an average of 0.23 ± 1.79 µg/kg dw. The concentration of ∑13PAEs detected in green mussel samples ranged from 35.74 - 1747.16 µg/kg ww with an average level of 523.93 ± 595.29 µg/kg ww. The concentration of ∑13PAEs in sediment ranged from 47.16 – 295.48 µg/kg dw, with an average of 144.32 ± 81.53 µg/kg dw. For all samples, ∑5PBDEs accumulated in green mussels ranged from 0.06 – 23.50 µg/kg ww, with an average of 8.60 ± 9.44 µg/kg ww. Concentrations of ∑5PBDEs accumulated in sediments ranged from 0.06 – 7.26 µg/kg dw and averaged 1.99 ± 2.43 µg/kg dw. The bioaccumulation coefficient for each compound (BPA, PBDEs, and PAEs) for the BSAF results of BPA at the study sites ranged from 108.03 to 584.47, the average value being 286.24 ± 198.95.

3. The accumulation of MPs in the soft tissue of green mussels had a low statistical correlation with the concentrations of BPA (r = 0.14) and PBDEs (r = 0.37) or no relationship was detected. between the accumulation of MPs and PAEs (r = -0.22) in green mussels was evaluated.

Request:

- Additional samples were taken at points deeper in the continent at emission points according to main discharge points and large flows to evaluate the ability to disperse MPs and chemicals spatially.

- Experimental study evaluating the bioaccumulation ability of green mussels for MPs and chemicals in artificial environments over time.

- Further research to clarify the mechanism of influence of

accumulation level on growth and development ability and the biological behavior of green mussels when exposed to several chemicals often added during the plastic production process at different times and concentrations.

NEW CONTRIBUTIONS OF THE THESIS

Initially, we quantified the quantity, shape, size, and composition of MPs and some typical organic substances accumulated in green mussels *(Perna viridis)*, seawater, and sediments in the coastal waters of Quang Ninh province. The thesis has determined the correlation between microplastics and several related organic substances and the level of accumulation and risk of MPs and organic substances based on the chemical toxicity indexes of polymers and PLI load. , bioaccumulation - sediment. The results obtained in this study can be a basis and reference for further studies on plastic pollution, especially studies on plastic pollution in organisms and its impact on the health of people in Vietnam.

Initial research results on BPA, PAEs, and PBDEs accumulated in green mussels *(Perna viridis)* in the coastal area of Quang Ninh have shown that BPA concentrations in green mussels are quite high compared to many other regions in the world and coastal sediment samples. From there, it shows that the accumulation of BPA, PAEs, and PBDEs is related to the accumulation of MPs in the environment in green mussels in the coastal area of Quang Ninh.

Initially, the green mussel *(Perna viridis)* can be identified as a bivalve species suitable as a biological indicator for assessing contamination by microplastics and other related substances in the coastal marine environment shore of Vietnam.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

1. Van Manh Do, Van Tuyen Trinh, Xuan Thanh Thao Le, **Duy Thanh Nguyen**, *"Evaluation of microplastic bioaccumulation capacity of mussel (Perna viridis) and surrounding environment in the North coast of Vietnam",* Marine Pollution Bulletin 199 (2024) 115987, doi.org/10.1016/j.marpolbul.2023.115987, SCI, Q1.
2. **Duy Thanh Nguyen**, Xuan Thanh Thao Le, Van Tuyen Trinh, Van Manh Do, *"Evaluation of chemical exposure to the sediment and green mussels (Perna viridis) at some coastal sites in Northern Vietnam",* Regional Studies in Marine Science 71 (2024) 103413, doi.org/10.1016/j.rsma.2024.103413, SCIE, Q2.
3. Xuan Thanh Thao Le, **Duy Thanh Nguyen**, Minh Tuan Pham, Minh Viet Trinh, Phuoc Cuong Le, Van Manh Do, *"Risk assessment of microplastic exposure: A case study near a refinery factory at the central coast of Vietnam",* 2023, Marine Pollution Bulletin, ISSN: 0025-326X, SCI, Q1.
4. Van Manh Do, Thi Thom Dang, Xuan Thanh Thao Le, **Duy Thanh Nguyen**, Thi Vi Phung, Dinh Ngo Vu, Hung Viet Pham, *"Abundance of microplastics in cultured oysters (Crassostrea gigas) from Danang Bay of Vietnam"* Marine Pollution Bulletin, 2022, ISSN: 1879-3363, SCI, Q1.
5. Xuan Thanh Thao Le, Minh Viet Trinh, **Duy Thanh Nguyen**, Van Manh Do, *"Overall evaluation of microplastic exposure in oysters (Crassostrea gigas) in coastal areas of Viet Nam"*, 2024, Regional Studies in Marine Science, ISSN: 2352-4855, SCIE, Q2.
6. **Nguyen Duy Thanh**, Vo Anh Thu, Dang Thi Thom, Duong Tuan Manh, Pham Minh Tuan, Le Xuan Thanh Thao, Vu Dinh Ngo, Trinh Van Tuyen, Do Van Manh, *"Investigation of microplastics existence in mussel (Perna Viridis) from Halong bay, VietNam",* 2022, Vietnam Journal of Science and Technology, ISSN: 2525-2518, SCOPUS, Q4.
7. Do Van Manh, Dang Thi Thom, Le Xuan Thanh Thao, **Nguyen Duy Thanh,** Duong Tuan Manh, Pham Hung Viet, *"Microplastics accumulation in Pacific oysters from Danang Bay, Vietnam",* Vietnam Journal of Science and Technology, ISSN: 2525-2518, SCOPUS, Q4.
8. Le Xuan Thanh Thao, Huynh Duc Long, Nguyen Thi Linh, Vo Anh Thu, Dang Thi Thom, **Nguyen Duy Thanh**, Do Van Manh, *"The evidence of microplastics exposure in Le Thuy beach of Quang Ngai, Viet Nam",* 2023, Vietnam Journal of Science and Technology, ISSN: 2525-2518, SCOPUS, Q4.
9. Le Xuan Thanh Thao, Huynh Duc Long, **Nguyen Duy Thanh**, Do Van Manh, *"Overview of sample processing methods in the microplastic analysis process",* 2021, Journal of Chemical, Physical and Biological Analysis, ISSN: 0868-3224.
10. Do Van Manh, Dang Thi Thom, Le Xuan Thanh Thao, **Nguyen Duy Thanh**, Huynh Duc Long, Nguyen Thi Linh, Doan Thi Thuy Linh, Vu Dinh Ngo, Duong Hong Anh, Pham Hung Viet, *"Analyzing the characteristics of Microplastic waste in beach sediments in coastal areas of Vietnam: Initial research in Da Nang"*, 2021, Vietnam Journal of Science and Technology, ISSN 2615-9759.