

VNU Journal of Science: Earth and Environmental Sciences



Journal homepage: https://js.vnu.edu.vn/EES

Original Article

Analyze and Compare the Microplastic Pollution in the Water Samples at Han River Estuary (Da Nang)

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Received 27th August 2024 Revised 11st November 2024; Accepted 12nd February 2025

Abstract: The aim of this is study to analyze and compare the amount of microplastics in the surface water and water column samples at Han River estuary (Da Nang) in the rainy season 2023. Sixteen water samples (eight water column samples and eight surface water samples) were collected and analyzed to determine the quantity, shape, color, size, and polymer forms of microplastics. The results showed that microplastics were present in almost all samples and the column water samples have the tendency of pollution with higher densities. Microplastic pollution between two group samples was not consistent ranging from 49 to 489 particles/L in surface water and from 95 to 334 particles/L in column water samples. Location DN6 recorded the highest values in both samples with 489 and 334 particles/L in surface water and column water, respectively. Microfragment predominates with 60.13% in both samples. Sequently, microfibers observed account for 36 and 33,33%, respectively. The remaining shapes range from the lowest of 0.57% (surface water samples) to 5.17% (water column samples). The white color predominances and found of 45 and 52.3% for surface water and water column samples, respectively. The second most popular color is blue, followed by green, red and several other colors. The microplastic with size in 50-150 µm accounts

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https://doi.org/10.25073/2588-1094/vnuees.5220

for the highest proportion 665 and 715 particles/L, respectively. Similarly, the large sizes in 300 - 500 μ m account for the lowest proportion, only reaching total values of 90 and 80 particles/L, respectively. FTIR results showed that PET (Polyethylene Terephthalate) polymer has the highest density in both two samples with 750 and 310 particles/L, followed by nylon with values of 140 and 175 particles/L, respectively. The remaining polymers such as Cellophane, Polystyrene standard, Teflon, Fluoropolymer, Urea fomaldehyde etc., account for a fairly low proportion and it is different between two groups of samples.

Keywords: Microplastic pollution, Han River estuary, water surface, water column.

1. Introduction

Plastic has become indispensable due to its characteristics including versatility, low price, long life, used at a wide range of temperatures, biologically inert and is very durable. This has led to plastics being applied in many sections such as household, personal goods, clothing, packaging and construction materials. As a result, global plastic production has increased exponentially since the mass plastic production was first implemented in the 1950 s and increased linear to 288 million tons in 2012 [1]. While a portion of plastic waste is properly managed and treated (through incineration or recycling), it is estimated that millions of tons of plastic waste still exist (4.8 to 12.7 million tons in 2010) and causes marine environmental pollution. The waste plastic decomposes into microplastics that accumulate in water, sediment, organisms and become a major hazard, affecting the environment, ecosystem and human health [2].

According to the US National Oceanic and Atmospheric Administration (NOAA) "microplastics are very small pieces of plastic less than 5 mm in size, which can enter natural ecosystems from a variety of sources including cosmetics, clothing, and industrial processes" [3]. Microplastics are divided into two groups: microplastics primary and secondary microplastics. Due to their small size, microplastics are easily confused with the food of living organisms [4]. The rivers significantly contribute to microplastic pollution in the oceans due to their estuarine directly connection to the sea. According to MONRE report (2021) it is

estimated that about 80% of marine waste comes from activities on land in Vietnam [5]. With 112 coastal estuaries stretching from North to South, it is potential pose the plastic waste to drift into the ocean and cause many risks affecting to the quality of the aquatic ecological environment in the estuary area.

Currently, many studies have been carried out to assess microplastic pollution but mainly in marine and coastal sediment [6-8]. Luu et al., (2020) recorded an average microplastic concentration of $22.95 \pm 8.9 \text{ mg/kg}$ at the tidal flats of Da Loc commune, Hau Loc district, Thanh Hoa province, in which microplastics in the form of fragments, pellets, fibers and films [6]. Similarly, when decomposing surface sediment samples of Tien Yen Bay, microplastic pollution was recorded of 664±68 MPs/kg, including fragments (8.54%), pellets (4.99%), fibers (84.9%), films (1.57%) and mainly PE, PVC, PP, PS, PA groups, etc,... [7]. In addition, microplastics have appeared in sediments in the Nhieu Loc - Thi Nghe canal due to plastic waste discharged into the environment [8]. These studies have provided important initial information about the status of microplastics in the sediment environment in general and the pollution of MPs in water body in particular. However, the database in the South-Central region is still quite limited. Therefore, this study was condcuted to analyze and compare the amount of microplastics in the surface water and column water samples at Han River estuary (Da Nang) in the rainy season 2023 for assessing the current status of microplastic pollution in the water environment, as a database basis for further scientific research.

2. Methodology

2.1. Sampling Area

Da Nang is the most important city of the Central region, located in the South-Central region, Vietnam. This city is one of the centers about economic, financial, political, cultural, tourism, social, educational, scientific and technological. Da Nang city has a geographical location stretching from 15055' to 16014' North and from 107018' to 108020' East. Han River is one of the four main rivers of Da Nang city, located downstream of Thu Bon River and plays an important role in the socio-economic development of Da Nang city. The 8 locations selected from Tien Son bridge running gradually towards Da Nang Bay (Figure 1). These are locations with many waste sources or activities related to the discharge of plastic and microplastic waste.



Figure 1. Map of sampling locations at Han River estuary - Da Nang.

2.2. Sampling Method

The process of collecting microplastic samples in surface water and water column was based on published methods [9, 10]. Neuston mesh set (with mesh hole size of 300 µm) was attached to the water collection box or Manta trawl net (dimensions $D \times W \times H = 30 \times 30 \times 15$ cm). A flowmeter attached to calculate the amount of water collected when microplastics flowed through the net. Sampling devices were anchored to boats at sampling locations and water collection boxes were floated on the water surface to collect all solid objects floating in the surface water layer and water column including plastic waste and other types of solids. Neuston net casting time was from 30 - 60 minutes. The sample collection time in this study is in the rainy season of 2023. Samples were stored at 4 °C in dark bottles and transported to the laboratory the same day.

2.3. Analysis and Statistical Methods

The samples were transported to the laboratory for analysis (density, shape, size and color) using a microscope MSZ5000-T-IL-TL, Kruss (Germany), then a Micro-FTIR system (Nicolet iN10MX) was used to classify the polymer forms present in the sample. The analysis procedure followed the published steps by Do et al., (2022) [11]. The data in the study is processed using GraphPad 6 software. The volume of water will be recorded on the flowmeter for calculation. Microplastic density is calculated according to the following formula:

$$C = \frac{\pi}{V}$$

Where is C: The microplastic density (fragment, fiber, particle/ m^3); n: Number of microplastic pieces in the sample (fragment, fiber, particle); V: Volume of water filtered through the mesh (m^3).

No.	Sampling area	Code sample	Characteristic			
1	Tien Son Bridge	ÐN1 (1602'8"B; 108014'8"Ð)	On both sides are residential areas of My An, Hoa Cuong Bac and Hoa Cuong Nam Ward, Ngu Hanh Son District.			
2	Tran Thi Ly Bridge	ÐN2 (1602'58"B; 108013'47"Ð)	On both sides are residential areas, restaurants near the Green Island villa area and Dinh Tien Hoang primary school in Binh Thuan Ward.			
3	Rong Bridge	ÐN3 (1603'38"B; 108013'38"Đ)	On both sides are residential areas and many restaurants in An Hai Tay and Hai Chau 1 Ward.			
4	Han river Bridge ĐN4 (1604'19' 108013'36"Đ)		On both sides are hotels, restaurants and supermarkets in An Hai and Son Tra Ward, Hai Chau and Son Tra District			
5	The discharge drain of city	ÐN5 (1604'47"B; 108013'34"Ð)	This is the discharge point from Da Nang city into Han River, near Da Phuoc (Old) fishing port and Da Nang marina in Thuan Phuoc and Hai An Bac ward.			
6	Thuan Phuoc Bridge	ÐN6 (1605'39"B; 108013'11"Ð)	This area is near Thuan Phuoc lighthouse, on both sides are hotels and restaurants, no population, in Thuan Phuoc and Nai Hien Dong Ward.			
7	On the Da Nang Bay	ÐN7 (1606'14"B; 108013'8"Ð)	This area is the intersection of the Han River flowing into Da Nang Bay, far from Thuan Phuoc bridge (ĐN6) 700 m.			
8	On the Da Nang Bay	ÐN8 (1606'1"B; 108012'50"Đ)	This area is far 800 m from ĐN7, on Da Nang Bay and there is no population.			

Table 1. Sampling location characteristics

3. Result and discussion

3.1. The Microplastic Density Classification by Quantity

The results in Table 2 showed that all 8 sampling locations have the presence of microplastics, ranging from 49 to 489 particles/L in surface water and from 95 to 334 particles/L in column water samples. The lowest microplastic density was recorded at location DN8 in water column samples and DN4 in surface water samples (49 and 95 particles/L, respectively). The highest value obtained at location DN6 for both water column and surface water samples (334 and 489 particles/L, respectively).

3.2. The microplastic Density Classification in Size

Microplastic samples are classified into 5 size groups including 20-50; 50-150; 100-300; 300-500 and >500 μ m (Table 3). The size in 50-150 μ m accounts for the highest proportion of 665 and 715 particles/L, respectively. Similarly, the large size in 300-500 μ m account for the

lowest proportion, only reaching total values of 90 and 80 particles/L, respectively. Location DN6 observed the microplastic density with values of 310 and 190 particles/L, respectively (sizes in 50-150 µm). There were no microplastics in surface water and water columns in locations DN4 and DN8, corresponding to the size 300-500 µm and 150-300 µm.

3.3. The Microplastic Density Classification in Shape

There are 4 forms of microplastic shape in both two sample groups at the Han River estuary (Da Nang) including: fiber, fragment, particle and other forms. Microplastic fragments were the most abundant form found in the study area in both surface water and water column samples with the highest value of 60.13%. Sequently, microplastic fibers observed account for 36 and 33,33%, respectively. The difference values also appear in the remaining two forms, particle and some other shapes, ranging from the lowest 0.58% (surface water samples) to 5.87% (water column samples) (Figure 2).

3.4. The Microplastic Density Classification in Colour

Microplastics colors are very variation (white, black, blue, green, etc,...). The white color is the most common and consistently present in all surveyed locations, accounting for 45 and 52.3% in surface water and water column samples, respectively. The second most common color is blue with values of 25.4 and 20.2%, respectively. Sequently, the green, red and some other colors recorded corresponding values in surface water samples as 15.9; 9.4; 4.3% and in the water column samples are 15.9; 7.1; 4.5% (Figure 3).

No.	Code	Number of microplastic (Particles/Lit)			
	sample	ĐN_NM	ĐN_CN		
1	ÐN1	50	171		
2	ĐN2	220	194		
3	ĐN3	49	142		
4	ĐN4	49	187		
5	ĐN5	108	137		
6	ĐN6	489	334		
7	ÐN7	92	148		
8	ĐN8	144	95		
]	Fotal	1201	1408		

Table 2. Total of microplastics in surface water (ĐN_NM) and water column (ĐN_CN) samples at Han River estuary (Da Nang)

Table 3. The size of microplastics in surface water (ĐN_NM) and water column (ĐN_CN) samples at Han River estuary (Da Nang)

Code	20-50 µm		50-150 μm		150-300 µm		300-500 µm		> 500 µm	
sample	ÐN_NM	ÐN_CN	ÐN_NM	ÐN_CN	ÐN_NM	ÐN_CN	ÐN_NM	ÐN_CN	ÐN_NM	ÐN_CN
ÐN1	10	30	25	80	5	20	5	30	5	20
ĐN2	35	70	110	90	45	20	15	10	20	15
ĐN3	20	40	10	95	5	20	10	15	5	20
ĐN4	15	80	25	70	10	15	0	10	5	25
ĐN5	45	35	35	55	20	25	15	10	5	20
ĐN6	60	115	310	190	55	40	25	5	50	10
ĐN7	20	15	50	95	15	30	5	10	15	5
ĐN8	35	45	90	40	0	10	5	0	25	10
Total	240	430	655	715	155	180	80	90	130	125



Figure 2. Average proportion of microplastic forms (fibres, fragment, particle and other forms) in surface water samples (a) and water column samples (b) in Han River estuary (Da Nang).



Figure 3. Microplastic colors in different locations: a) Surface water sample; b) Water column sample.



Figure 4. The polymer ratio of microplastics in different locations: a) Surface water; b) Water column.

3.5. The Microplastic Density Classification by Polymer Forms

There are 18 and 22 polymers with a total of 1220 and 1501 particles/L found in two groups of samples. PET polymer recorded the largest amounts with values of 750 and 310 particles/L, respectively. The second most popular polymer is nylon with values of 140 and 175 particles/L, respectively. In addition, Olefin and Polyester are two types of polymers that appear in 4 - 5 locations in surface water samples with a total amount of 50 and 45 particles/L, respectively. The remaining polymers such as Cellophane, Polystyrene standard, Teflon, Fluoropolymer, Urea formaldehyde, HDPE etc,... appear from 1 to 3 sampling locations (Figure 4). In contrast, Polypropylene, Olefin, Cellophane and Melamine are three types of polymers that appear in 4 - 5 water column sampling locations with total amounts of 16, 50, 30 and 35

particles/L, respectively. The remaining polymers such as Polyethylene, Polypropylene Homopolymer, Evoh Eval Film, LDPE, PVC etc,... were only found in 1 - 3 locations (Figure 4).

3.6. Discussion

The results of this study are also similar to some previous works in the estuary area [12]. To study the transport cycle from source to estuary, Lenaker et al., (2019) showed that there is always a tendency for microplastic pollution with different concentrations and densities in surface layers higher than the water column layers in estuaries, harbors or reservoirs. The density also decreases with depth in the water column layer and deposited into the sediment [13]. Compared to plastic debris, microplastics are more likely to harm organisms because they are mistaken for their food [4]. When plastic exists in the environment for a long time, the large microplastics can decompose into smaller microplastics under the influence of factors such as sun, wind, flow speed,...

The data obtained showed heterogeneity in the shape and size of microplastics in the water samples. Fiber and fragment were dominant in all 8 surveyed locations, followed by particles and other shapes. The size ratio observed < 150µm is predominating (Table 3), it showed that the water environment in the study area receives a large source of plastic waste in a long period of time. Due to microplastics with lower densities and smaller sizes, they will increase their potential transport by wind and water, leading gradually increasing their ability to accumulate in the environment. Because microplastics can easily be mistaken for food by aquatic organisms [4], the color of microplastics is also a special concern in the aquatic environment. The color of microplastics is expected to provide information about their original sources, such as packaging materials [14] or cosmetic products [15]. However, some colorless or transparent microplastics may be missed during extraction or identification.

According to Lebreton et al., (2017), microplastics enter the marine environment mainly through rivers due to some physical characteristics such as depth, wind direction, water flow,... [15]. This is consistent with the results obtained at location ĐN6. This location has a large water surface area, high depth, and strong wind, so the hydrodynamics of river water and surface flow have affected the distribution of microplastics at this location. The total density in the water column samples in the study area is also higher than in surface water, which can be explained by the fact that surface flow is the main mechanism by which microplastics are transported in water along the river and into ocean [16]. On the other hand, microplastic density is also affected by the tidal regime and weather. In this study, samples were collected during the rainy season, which according to the summary records in Asia and East Asia, up to 474.5% of the total amount of plastic waste discharged from rivers occurs between May and

October each year [15]. The analysis results are similar to many studies in the region and are explained by the impact of the East Asian monsoon.

The FTIR spectral analysis results also confirm the previously published results on microplastics in water. PET and PP are two common polymers with a wide distribution in freshwater, estuarine and marine environments [17, 18]. The proportions of PET and PP detected in the Yangtze River estuary (China) by Li et al., (2020) [17] were 37.3 and 28.6%, respectively, or Diana et al., (2022) also recorded PET in the Sado River estuary (Portugal) at 41% [18]. Currently, microplastics are widely distributed in aquatic, sedimentary and biological environments, data on the distribution and accumulation of this type of pollution plays an important role in ecological risk assessment. Therefore, further studies are needed to classify plastic groups and there needs to be policies to reasonably manage the use of plastic products in daily life, transportation, etc., to limit microplastic pollution in the ecosystem.

4. Conclusion

The study analyzed and compared microplastic characteristics according to quantity, shape, size, color and polymer type in water samples at Han River estuary (Da Nang). The results showed that microplastics appear in all surveyed locations and there is heterogeneity between the two types of samples (the column water higher than surface water samples). Microfragment and microfibers with small sizes are predominant. The main color is white, followed by blue, green, red and other colors. The research results also showed that residential activities and civil on both sides affect the appearance of microplastics in the survey locations.

The results obtained in this study are basic data on the status of plastic pollution in the Han River estuary in particular and the South-Central Coast estuary in general. As one of the tasks of the national project, this result is the basis for carrying out the following tasks such as assessing the toxicity of microplastics on organisms in the aquatic and sedimentary environment and studying the effects of physical characteristics of microplastics on distribution and transport in the environment.

Acknowledgments

This article is the result of project KC562, code DTDL.CN÷53/22 "Research and assessment of the accumulation and impact of microplastics on the estuarine ecosystem along the South-Central Coast". The authors sincerely thank the Ministry of Science and Technology for providing funding to carry out the project and this article.

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