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Preliminary results on microplastics in surface water from the downstream of the Day River

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ABSTRACT

Microplastics (MPs), referring to plastic items ranging from 1 to 5000 µm long, are polluting the terrestrial and aquatic environments and are becoming a threat to the health of ecosystems, biota and humans. Rivers are major carriers of these materials from the terrestrial environment to the oceans. In the present study, the occurrence of MPs in a peri-urban river was investigated. The Day river system is a good example of a peri-urban river strongly influenced by human activities in the whole basin. Water samples were collected from the downstream of the Day River, including Cau Que, Cau Do and Do Thong, in the rainy and dry seasons using a plankton sampling net for identifying microplastic concentration, size, shape, color and polymer composition. Microplastic abundance in the surface water ranged from 269,693±60,624 to 863,005±131,925 items/m^3. The microplastic concentration in the rainy season was higher than that in the dry season. Microplastic abundance was increased at a site near urban areas with high human activity. The microplastic shape was collected in different seasons did not change significantly, with microplastic fibers as the major items, accounting for above 92% of the total items. Many fiber microplastics collected in this study were in small sizes of 300-1000 µm and 1000-2000 µm, occupying 78.5-85.7% of the total microplastic items. Purple was the most common color of microplastics. Polyethylene (PE) and polypropylene (PP) were major polymer types of the selected items in the surface water samples downstream of the Day River.

Keywords: microplastic, fiber, Day River, surface water, Vietnam.

1. Introduction

Plastic pollution is a threat and a challenge that the environment, global economy, and society are facing together. Vietnam is in the top 4 of 20 countries with the highest plastic waste in the ocean (Jambeck et al., 2015). Plastics are synthetic or semi-synthetic organic polymers with high molecular weight

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which are used as raw materials to manufacture a wide variety of everyday items, closely related to modern human life and industrial products. The origin of plastics mainly comes from petrochemical products (Thompson et al., 2004). Due to its low cost, ease to manufacture, flexibility, waterproof, lightweight, high endurance, plastic is utilized in numerous areas of life such as packaging, construction, transportation, medical, home electrical appliances, electronic equipment, toys, manufacturing designs, toys, agriculture, etc.… With its structural characteristics of synthetic polymers, plastic waste has a prolonged decomposition rate and can remain in the environment for hundreds of years. Plastics can be dispersed in the environment by wind and water currents (Thompson et al., 2004). Therefore, plastic waste is currently a common pollutant in multiple ecosystems throughout the world. According to statistics, only a minor part of used plastic products was collected for recycling or reuse, while most of them are discharged directly into the environment. Statistics also show that 60 to 80% of marine waste is plastic waste, and there are about 8 million tons of plastic waste ending up in the ocean every year (Derraik, 2002; Geyer et al., 2017). Marine plastic waste mostly comes from beaches, marine transportation, aquaculture and land (urban wastewater or river flows).

The occurrence of microplastics in the ocean was discovered in the early 1970s. The microplastic term was proposed in 2004 and quickly attracted the attention of scientists. MPs are tiny plastic particles that are difficult to observe with the naked eye because their size diverts from 1 µm to 5 mm with unique shapes such as fibers, fragments and granules (Geyer et al., 2017). Depending on their origin, microplastics are divided into 2 groups: primary and secondary microplastics. Primary microplastics consist of: (i) plastic pellets used as raw materials in the manufacture of plastics. Besides, plastic pellets are also used in diverse industrial applications as ingredients in printing inks, spray paint, textile particles, drugs, cosmetic and body care products; (iii) plastic items used in surface abrasion. Secondary microplastics are the product of broken plastic debris in the environment under mechanical, chemical and biological impacts. The secondary plastic sources include fishing nets, industrial plastic pellets, household plastic items and other broken plastic pieces. The fragmentation of the resin into microplastic particles results from different decomposition processes that lead to the accumulation in the environment. Secondary microplastics are believed to be the major contributor to microplastics in the environment.

Until recently, there have been only a few studies on microplastic pollutants in Vietnam, e.g., a group of scientists from Ho Chi Minh City University of Technology - Vietnam National University Ho Chi Minh City carried out on the Saigon River (Lahens et al., 2018). In their study, the scientists found microplastics of various colors and shapes, mainly derived from polyethylene and polypropylene, while the artificial fibers were mainly polyester. In addition, the authors have identified microplastics with a majority size of < 500 micrometers. In another recent research, the result of microplastic accumulation in the green bivalve mollusk (*Perna viridis*), sampled in Thanh Hoa, reveals that the average density of microplastics was 2.6 items/individual and 0.29 particles/g FW. Six types of plastic (polypropylene, polyester, polyethylene, polystyrene, polyamide and PVA) have been identified, in which polypropylene (PP) and polyester accounted for 31% and 23%, respectively (Nam et al., 2019).

Overall, it can be seen that, though being one of the countries with the highest amount of plastic waste to the ocean, researches on plastic waste pollution in general and microplastic pollution, particularly in Vietnam, is still minimal. This study presents the initial research results on the abundance and characteristic of microplastics in the surface water of the Day River downstream.

2. Material and Methods

2.1. Sampling location

To assess the level of microplastic pollution of the water environment in the Day River's downstream, three sampling locations (Cau Que, Cau Do and Do Thong) were selected to collect samples during the rainy season in June and August 2020 and the dry season in December 2020 and January 2021. The chosen locations are presented in Fig. 1, Table 1.

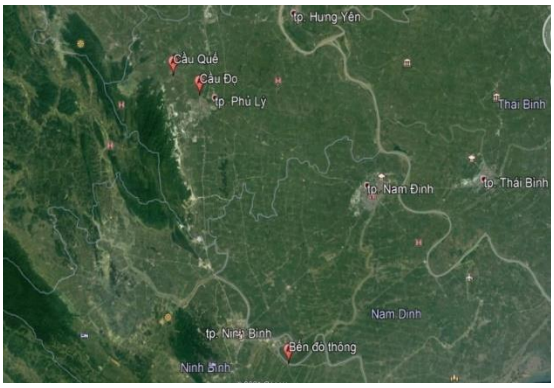


Figure 1. Location of sampling sites in the downstream of the Day River

Table 1. Location of sampling sites in the downstream of the Day River

No.	Locations	Sampling location information	Longitude	Latitude
1	Cau Que	Located in Que town, Kim Bang district, Ha Nam province, to assess the water of Day River before receiving wastewater from Hanoi via the Nhue River.	20.5745	105.8726
2	Cau Do	Located in Thanh Chau commune, Phu Ly city, Ha Nam province, represents of the Day River after receiving water from the Nhue River.	20.5158	105.9115
3	Do Thong	Located in Khanh Cu commune, Yen Khanh district, Ninh Binh province, represents of the Day River.	20.2174	106.0451

2.2. Sampling method and sample analysis

Surface water samples were taken at the 3 sampling sites from June 2020 to January 2021 (June, August, December 2020 and January 2021) using an 80 µm mesh size plankton net (50 cm diameter) coupled to a flowmeter (General Oceanics®) to determine the sampled water volume. The net was exposed from 2 to 5 minutes, equivalent to 0.21 to 0.7 m^3 according to sites and sampling periods. A total of 36 water samples were collected during the sampling period and the average values of microplastic concentration were presented. The net was sunk below the water's surface for 5 minutes; then, it was washed from the outside while the inside of the net was collected into a 500 ml glass bottle, then kept cold at -4°C until analyzed. At each sampling site, surface water samples were collected in triplicate. Garbage (plants, wood and shells) in the water samples with the size >1 mm was removed through sieving. The microplastics in the water samples <1000 µm in size were retained in 500 ml glass bottles and treated using Sodium Dodecyl Sulfate (SDS, Merck®) at 50°C for 24 hours, biozym SE (protease and amylase) and biozym F (lipase) at 40°C for 48 hours and hydrogen peroxide (H_2O_2 30%, Merck®) at 40°C for 48 hours. After the above chemical treatment, the samples were transferred to a sieve with a mesh size of 250 µm: the fraction < 250 µm part was discarded, and the one > 250 µm was kept in a clean glass beaker. A saturated NaCl solution was used to separate the microplastics. This step was repeated at least 5 times to ensure that all microplastics from the sample were collected. After separating, the solution containing microplastics was filtered through GF/A filter papers using a glassware filtration unit. The filter papers were stored in sterile Petri dishes until examined under a Leica MZ12 microscope. The morphology of fragments and fibers was measured using LAS software. Based on GESAMP recommendations, this study focused only on microplastics with a minimum length of 300 µm and plastic fragments with a minimum area of 45000 μm^2 or more. The chemical composition of the extracted microplastic items was identified on the Raman spectroscopy instrument (HORIBA XploRA Plus).

3. Results and Discussion

3.1. Seasonal variation of MPs in surface water in downstream of the Day River

So far, the research of microplastics in freshwater bodies has been less than in the marine environment. Some mainly focused on microplastics in large rivers and lakes. Rech et al. (2014) suggested that river basins are the main transition sites of plastic fragments from land to ocean, indicating that the transport of microplastics depends on the river flow. Series of investigations have documented microplastic contamination in freshwater bodies in several Americas, Europe, Asia, and Africa (Lechner et al., 2014; Kataoka et al., 2019).

In this study, the density of microplastics was observed in surface water samples in the downstream areas of the Day River, such as Cau Que, Cau Do and Do Thong. The research results showed that all water samples at all three sites contained microplastics. The average density of microplastics detected at the water sampling locations has a significant variation (Fig. 2), from 269,693±60,624 to 863,005±131,925 items/m^3. In terms of space, microplastic concentration was highest at Cau Do (863,005±131,925 items/m^3) because this location receiving a generous amount of wastewater from the inner city of Hanoi (where the population density is high), which flow through the Nhue River (Do Thu Nga and Trinh Anh Duc, 2020). This state led to a sudden increase in the density of microplastics at this site. At the Do Thong site, the lowest density of microplastics (269,693± 60,624 items/m^3) was due to this area's low population density, resulting in less discharged wastewater. A statistically significant difference ($p<0.05$) in the concentration of microplastics between Cau Que and Cau Do sampling locations compare to the Do Thong location. These results indicated that the concentration of microplastics in surface water tended to decrease gradually when flowing from places with high population density to low population density and/or probably due to the river dilution. The research by Kataoka et al. (2019) also reported that a larger number of microplastics was detected in densely populated areas along with industrial zones. High population density and human activities, urbanization, industrialization, tourism were proportional to microplastic in the environment. The microplastic concentrations identified in this study were higher than those in the Saigon River and urban canals through Ho Chi Minh City in previous studies (Lahens et al., 2018; Lahens et al., 2020). The textile industry greatly affects this river-estuary system, with an enormous density of artificial fibers identified from 22,000 to 251,000 items/m^3. Furthermore, the water flow rate of the section flowing through Cau Que and Cau Do was lower than Do Thong. Research by Joseph et al. (2018) has noted that hydrodynamics greatly influences the variation of the microplastic density. The deposition of sediments and microplastics was facilitated in places with low flow velocity, further explaining the results obtained in this study.

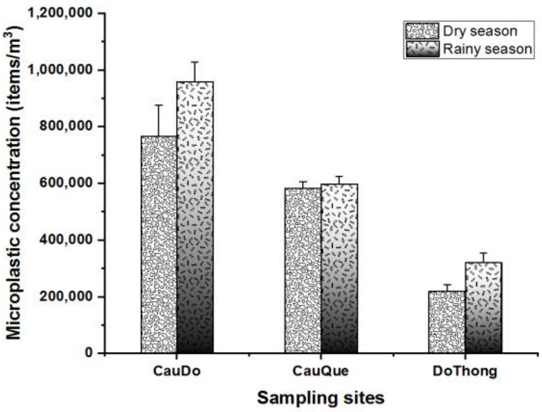


Figure 2. Mean microplastic density in water samples collected from the downstream of the Day River

In terms of time, the density of microplastics at the Cau Que location did not change between the rainy and dry seasons, possibly because the amount of rainwater flowing from the surface into the river at this area carried an insignificant amount of microplastic (Fig. 2). Meanwhile, the most evident difference in the microplastic density based on seasons was detected in Do Thong with 218,720±23,010 items/m^3 in the dry season and 320,667±33,427 items/m^3 in the rainy season. At the Cau Que and the Cau Do sites, the microplastic concentrations in the dry and rainy seasons were from 583,582±22,344 to 597,716±26,085 items/m^3 and from 767,596±107,551 to 958,414±69,052 items/m^3, respectively. The research results revealed that the microplastic density at Cau Do and Do Thong sites differed in terms of the seasons, demonstrating that weather conditions (rain) had a significant influence on the microplastic concentrations in the waterbody. In the rainy season, water samples had a higher microplastic concentration than in the dry season. The cause was that in the rainy season, rainwater from the surface dragged along a vast amount of microplastics into the rivers, contributing to the increasing density of microplastics. In the Nakdong River, Korea, the abundance of microplastics in the rainy season was also higher than in the dry season. The density of microplastics increased from 260 to 1,410 items/m^3 (dry season) up until 210 to 15,560 items/m^3 (rainy season) (Kang et al., 2015). The high density of microplastics in the rainy season has also been reported in Hong Kong (Fok and Cheung, 2015). Another survey of microplastics in two rivers of California (USA) with similar results displayed that microplastics ranged from 153 to 12,932 items/m^3. The authors also found that about 2.3 billion plastic items from these river systems ended up in the marine environment in 3 days (Moore et al., 2011). Our research results showed that the concentration of microplastics in the surface water in some downstream areas of the Day River (Cau Do, Cau Que, and Do Thong) was significantly high compared to the areas with good environmental quality, such as the Danube River, Austria or the Goiana River, Brazil (Table 2).

Table 2. Microplastic concentrations in surface water samples reported worldwide

Sampling locations	Mesh size of the net (μm)	The highest concentration of MPs (items/m^3)	References
Danube River, Austria	500	141.7	Lechner et al. (2014)
Rivers in Germany and Dutch channels	300	1.87×10^5	Leslie et al. (2017)
Three Gorges Dam, China	48	1.26×10^4	Di and Wang (2017)
Yangtze estuary, China	32	1.02×10^4	Zhao et al. (2014)
River in Los Angeles, USA	800, 500	1.29×10^4	Moore et al. (2011)
Estuary, Goiana, Brazil	300	0.19	Lima et al. (2014)
Cau Do, Day River, Vietnam	300	0.99×10^6	This study
Cau Que, Day River, Vietnam	300	0.61×10^6	This study
Do Thong, Day River, Vietnam	300	0.33×10^6	This study

The concentration of microplastics in surface water in some areas in this study was much higher than in the areas with severe plastic waste pollution, such as rivers in Los Angeles (USA) or some rivers in China, Germany or in Netherlands.

3.2. Microplastic composition in the downstream of the Day River

3.2.1. Shape and size of microplastics

Observing the microplastic samples using light microscopy with 100 times magnification on Whatman GF/A filter paper showed that the shape of microplastics at the three study sites of the Day River downstream were classified into two main groups: fiber and fragment. The fibers with a range of 92.55%-96.04% were dominant, compared to the fragments with 3.96% - 7.45% (Fig. 3).

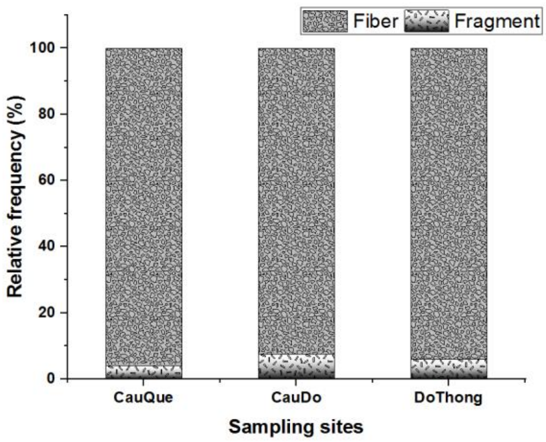
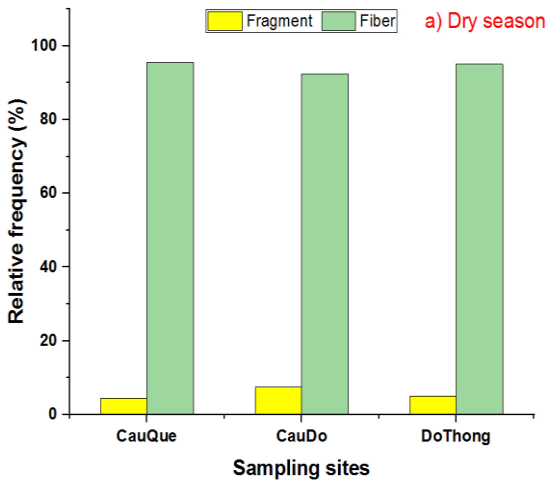


Figure 3. Relative frequency of microplastic items in surface water samples collected in the downstream of the Day River

The above classification was closely related to the shape of the microplastics. As known, fiber has a long and thin appearance; fragment microplastic is a small piece or part of a large plastic; pellets are in the form of an egg-shaped or a disc or a cylinder; the film is a piece of plastic that has a skinny layer; and styrofoam is a lightweight, elastic foam made from polystyrene. When the microplastics cannot be identified as fiber, fragment, film, or styrofoam, they are defined as fragments. The experimental data shown in Fig. 3 presents that microfiber plastics accounted for the major proportion of over 92%: Cau Que (96.04%), Cau Do (92.55%), Do Thong (94.01%); whereas fragments accounted for a minor proportion with the highest at Cau Do (7.45%) and the lowest was at Cau Que (3.97%). Fiber as the dominant shape in the water samples in this study was consistent with previous studies on urban rivers (Lahens et al., 2018; Lahens et al., 2020). In addition, fiber microplastics were also found in Peng et al. (2017) studies on the Truong Giang coast with 93%, or the Thames River, UK. Horton et al. (2017) suggested that the fiber shape of microplastics could be affected by human activities around the river. Microplastics in urban rivers can also be derived from the deposition of matter in the air (Dris et al., 2015), domestic wastewater (Browne et al., 2011), fishing ropes and nets (Zhang et al., 2015) or food bags (Wang et al., 2017). Microplastics are then transported to the aquatic environment by surface runoff from processing facilities or wastewater treatment plants, where they could not be removed entirely from the wastewater (Cole et al., 2011). This can also explain why many microplastics were found in the water at the sampling sites.

The variation of microplastic shapes over time (wet and dry seasons) was also monitored in this study.

The outcome in Fig. 4 shows that in water samples, microfibers dominated both the dry and rainy seasons, over 90%, while fragments accounted for a low percentage. In terms of time, the proportions based on shape in the study sites did not significantly change: at Cau Do and Cau Que, the proportion of fragments in the dry and rainy seasons were 7.60% and 7.29%; 4.49% and 3.43%, respectively. In two study sites, the proportion of microplastic fragments tended to decrease slightly in the rainy season. In the meantime, at the Do Thong site, the fragment proportion in the rainy season was higher (6.99%) than in the dry season (4.95%). Wang et al. (2021) also reported that microplastic fibers could originate from numerous sources, including clothes washing, the use and abrasion of plastic products and plastic waste generated in industrial production (Claessens et al., 2011; Browne et al., 2011). Furthermore, microplastic fibers can come from large plastic pieces susceptible to wind, water flow, temperature and erosion by hard substances during the movement (Peters and Bratton, 2016). Together with determining the shape of microplastics, this study also statistically conducted microplastic size in the collected water samples. The microplastic size varied between 300-5000 μm for fiber items and 50,000-2,100,000 μm^2 for fragment items.



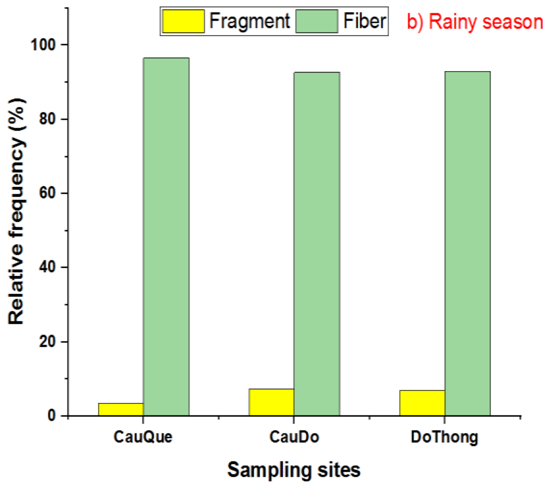


Figure 4. Seasonal variation of microplastic shapes in the downstream of the Day River

Observing the graphs, the fragment and fiber microplastics in the chosen sites were available in various sizes. At Do Thong, the fragments had an area of 56,593 μm^2 to 2,084,822 μm^2; the fibers had the size from 302 μm to 4,927 μm. At Cau Que, as for fragments from 58,636 μm^2 to 728,580 μm^2, as for the fibers from 302 μm to 4,756 μm; at Cau Do, as for fragments from 51,301 μm^2 to 922,609 μm^2, as for the fibers from 304 μm to 4,874 μm. The microplastics at the Do Thong site were larger than at Cau Que and Cau Do in both fragments and fibers.

The size distribution of microplastic fibers collected in this study was mainly divided into 300-1000 μm, 1000-2000 μm, 2000-3000 μm, 3000-4000 μm, and 4000-5000 μm as shown in Fig. 5a. These ranges represented the different sizes of microplastics found at the research sites. The occurrence frequency of microplastic fibers was mainly microplastics with the size of around 300-1000 μm (respectively 52.13% for Cau Do, 47.19% for Cau Que and 35.51% for Do Thong) and 1-2 mm (30.58%, 38.52% and 42.93%, correspondingly). Fiber microplastics with sizes ranging from 2000-3000 μm, 3000-4000 μm and 4000-5000 μm were at a low frequency of occurrence, in the variation of 1.28-15.90%.

Regarding the area distribution, microplastic fragments discovered in this study were mainly divided into the areas of 50000-100000 μ^2, 100000-200000 μ^2, 200000-400000 μ^2, 400000-900000 μ^2, and 900000-2100000 μ^2. In which, the frequency of appearance of microplastics in the locations of Cau Do, Cau Que and Do Thong in the above range of areas was 31.25%, 25% and 26.09%; 25%, 12.5% and 43.48%; 31.25%, 31.25% and 13.04%; 12.5%, 31.25% and 15.22%; 0%, 0% and 2.17%. In general, in this study, for the fibers, the microplastic particles with the size of 300-1000 µm and 1000-2000 µm are predominant with 78.45-85.71%. Similarly, the microplastic fragments with an area of 50000-400000 μ^2 also have a high 68.72-87.50% rate. This size distribution trend was similar to that of China's Yangtze River (Li et al., 2020), Germany's Elbe River (Scherer et al., 2020), where the highest frequency was 300-2000 µm, while large particles (2000-5000 µm) were rarely observed.

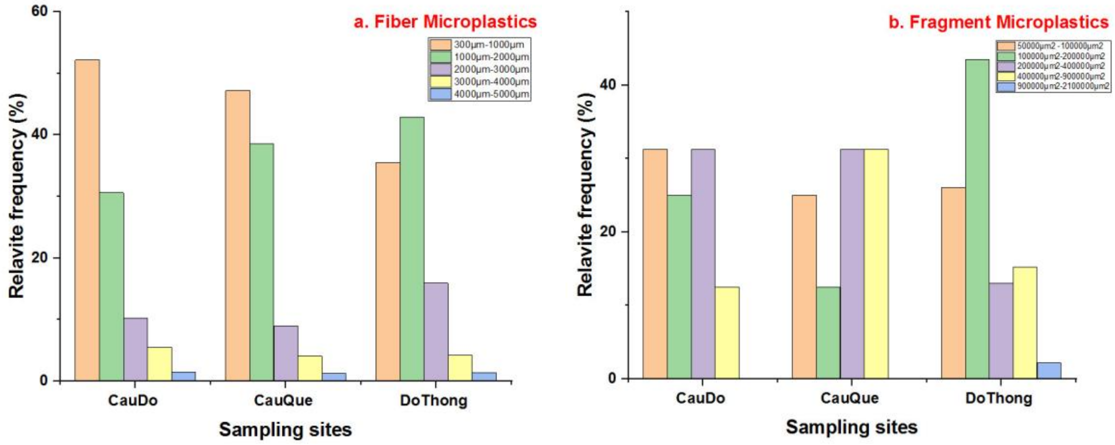


Figure 5. Size distribution of microplastics in the downstream of the Day River

3.2.2. The distribution of microplastic colors in surface water in the downstream of the Day River

The microplastic samples collected were classified by color in this study, with white, black, red, blue, yellow, green and purple (Fig. 6). In all 3 study locations, the results displayed that purple microplastic samples accounted for the highest percentage and had quite a wide fluctuation, specifically increasing gradually downstream, with 52.31% at Cau Que site, Cau Do with 55.45% and Do Thong up to 61.54%. In this investigation, the dominant purple color was possibly from clothing fabrics, plastic products from fishing equipment, packaging materials and domestic wastewater from washing clothes (Su et al., 2016). Other colors such as white, blue, red, green and sometimes yellow have been observed. The green microplastic samples tended to decrease with 33.19% at Cau Que, 14.69% at Cau Do and 11.30% at Do Thong. Blue also tended to reduce gradually downstream, while red did not follow any pattern. In contrast, some studies have declared that black and blue fibers were more common (Nuelle et al., 2014).

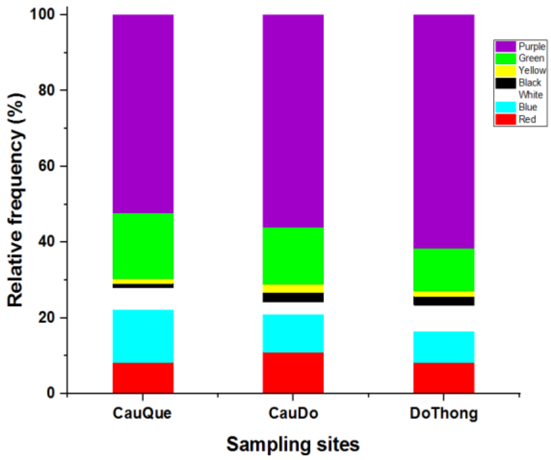


Figure 6. Color variation of microplastics in surface water in the downstream of the Day River

On the other hand, most of the microplastic fibers ingested by animals were black or blue (Duncan et al., 2019). In general, the color of microplastics collected was diverse in this study, with a large percentage of colored microplastics. Our results were similar to the research results of Wang et al. (2017), which showed that the microplastics in Wuhan urban surface water were mainly colored particles ranging from 50.4% to 86.9% of the total. The group also stated that the colored fibers derived from urban wastewater, commonly used in consumer products, were the most abundant microplastic fibers (Wang et al., 2017). This can be evidence for large amounts of colored microplastics in the above study sites (heavily affected by urban wastewater).

3.3. Polymer composition

Raman spectroscopy has known as the relevant technique for MP identification. The results of Raman spectroscopy showed that polyethylene (PE) and polypropylene (PP) were major polymer types of the selected items in surface water samples downstream of the Day River (Fig. 7).

Polyethylene (PE) is mainly used to manufacture plastic containers and packaging (Vianello et al., 2013). Polypropylene (PP) is commonly used in clothing, blankets and other fiber products, apart from food packaging, pipes and chemical containers (Wang et al., 2021).

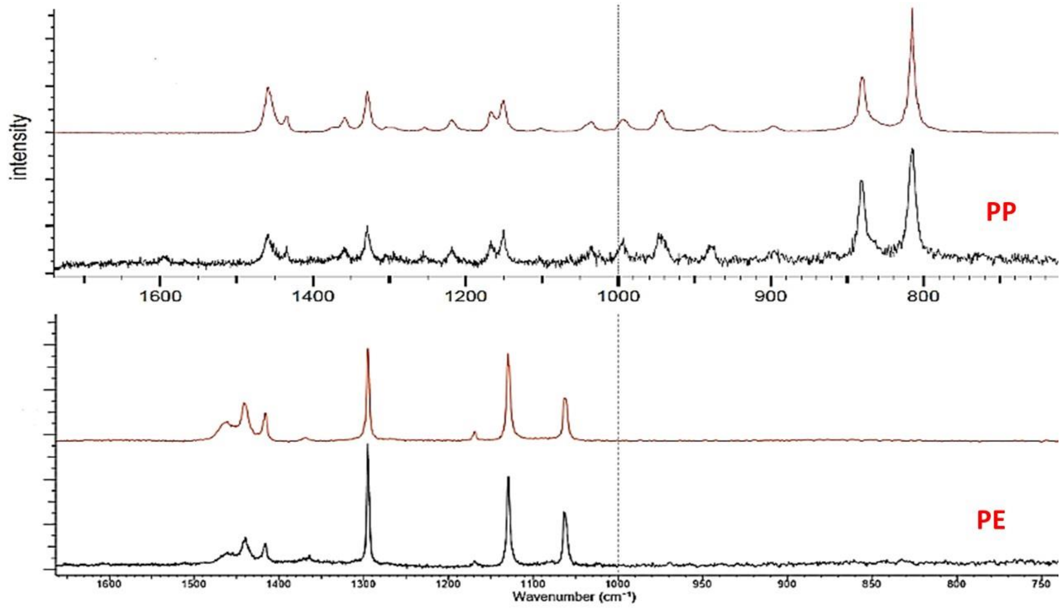


Figure 7. Raman spectrums of microplastic particles (PP and PE) found in water samples collected from the downstream of the Day River

4. Conclusions

Surface water samples collected from the three sampling sites of Cau Que, Cau Do and Do Thong downstream of the Day river contained microplastics with a relatively high concentration. The concentration of microplastics in the wet season was higher than those observed in the dry one. The shape of microplastics collected in different seasons did not change significantly, with microplastic fibers as the major in both seasons. The microplastics collected in this study were mainly small particles of 300-1000 µm and 1000-2000 µm, accounting for 78.5-85.7% with no significant seasonal change. Colored particles were dominant in the research samples. Polyethylene (PE) and polypropylene (PP) were major polymer types of the selected items in surface water samples downstream of the Day River. These data can support in controlling and solving microplastic contamination at specific sites and by region.

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