Microplastic characterization of sediment in Code River, Yogyakarta City

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Abstract. The purpose of this study was to determine the type, number and size of microplastics in the sediment and to compare each sample deposit in the Code River sediment. This research was conducted in June 2022 in Code River, Yogyakarta. Samples were taken by PVC pipes 10 cm deep, later analyzed in the laboratory. Fourier Transform Infrared (FT-IR) analysis was conducted to determine the plastic types based on the database of the functional groups. Samples in the Code River contained 2,423 particles of microplastic fragments, 721 particles of film, 322 particles of granules and 264 particles of fiber. The total number of microplastics in the Code River sediment from the upstream, middle and downstream zones was 3,730 particles kg^{-1}, of which 550 particles kg^{-1} in the upstream zone, 1,646 particles kg^{-1} in the middle zone and 1,534 particles kg^{-1} in the downstream zone. Microplastics in Code River sediments vary in size from small to large. The smallest size was found in the type of granule at station 2 with a diameter of 51 μm and the largest size was in the type of film at station 3 with a length of 117-1,563 μm. Microplastics in Code River sediments differed in number and size from each zone to another and even within the same sample point.

Key Words: microplastic, particle, river, sediments.

Introduction. Microplastics are plastics with small size like ≤ 5 mm. Microplastic waste has the potency to be toxic and dangerous when it enters the aquatic environment. The presence of microplastics in aquatic and sedimentary environments is largely caused by large plastic fragments which naturally decompose through sand grinding, wave action and other processes (Layn et al 2020). Boucher & Friot (2017) stated that photodegradation, biodegradation and thermal degradation may exacerbate the mechanical processes of plastic decomposition so that lots of microplastics are found in waters and even in sediments. Hidalgo-Ruz et al (2012) conducted a study on the identification of microplastics in waters, showing that the highest amount of microplastics was found in sediments rather than in the surface streams. Microplastics are found in waters and sediments, but the abundance of microplastics is the highest in sediments compared to waters, since microplastic transport tends to be slower in sediment (van Cauwenberghe et al 2015; Manalu 2017).

The Code River, as a river with an active volcano as the catchment area, has a lot of sedimentary material resulting from the past eruption of Merapi Volcano. Most of the suspended sediment load material that is carried by the river flow in the Code River comes from sediment from the 2010 Merapi eruption, but it is very likely that it can also carry other materials such as microplastics which originate from human activities on the river banks (Manalu 2017). Soil pollution that occurs on the banks of the Code River is a result of accumulation of indestructible inorganic waste like plastic, leading the formation of microplastics.

In this report we had identified the size, amount, and polymer types which were found on 6 different sampling site along the Code River. The sampling was primarily taken on the Yogyakarta City segment. Thus, this report provides the current profile of microplastic pollution on Yogyakarta City segment of Code River in 2022.

Material and Method

Description of the study sites. The research was conducted on June 2022 in Code River, especially along the Yogyakarta City (Table 1 and

Figure **1**). There were 3 main areas, upstream, middlestream, and downstream. Each area was divided into 2 different sampling sites. Thus, in total there were 6 sampling sites, as the coordinates were stated in Table 1.

Table 1

Sampling sites and their coordinates

Sampling site code	*Location*	*Coordinates*	*Distance from T6 (km)*
T1	New Bridge in Gadjah Mada University	7°45'44.35"S 110°22'14.55"E	7.04
T2	Dr. Sardjito Hospital	7°46'6.50"S 110°22'14.45"E	6.19
T3	Gondolayu Bridge	7°47'0.78"S 110°22'15.45"E	4.17
T4	Kéwék Bridge	7°47'29.56"S 110°22'6.67"E	3.13
T5	Mergangsan Dam	7°48'23.14"S 110°22'27.38"E	1.20
T6	Pratama Hospital	7°49'0.62"S 110°22'28.19"E	0.00

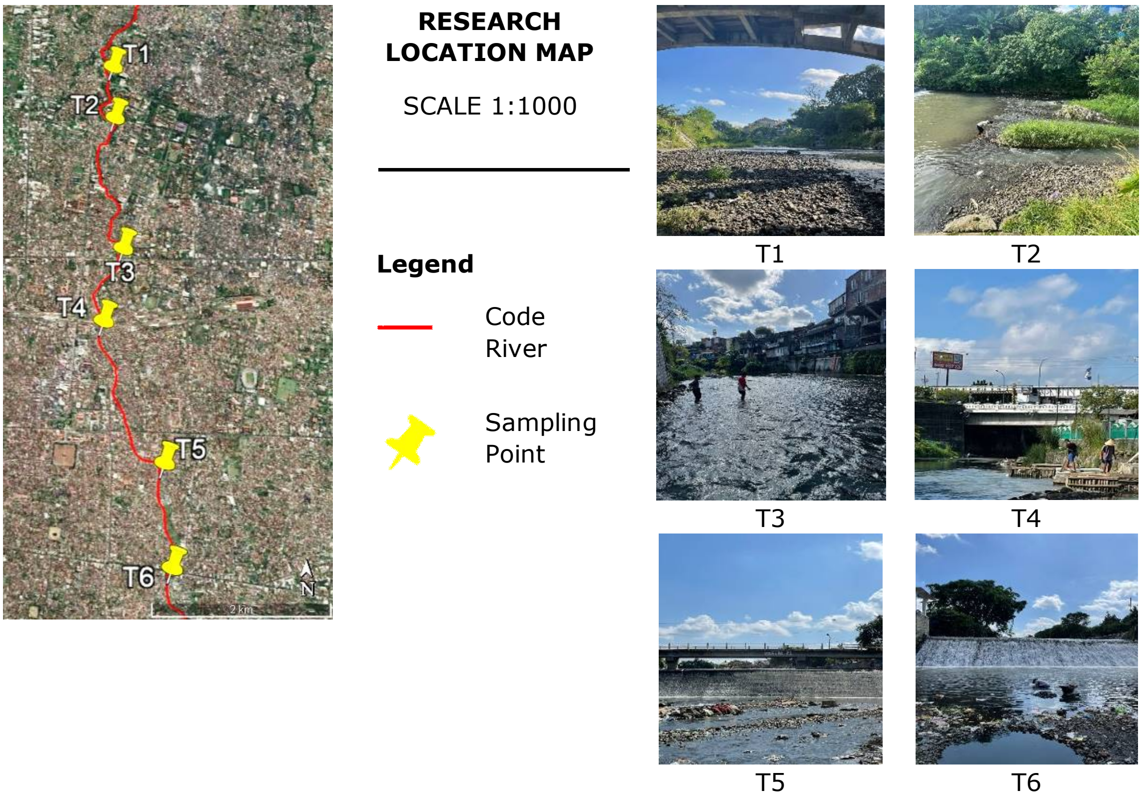

Figure 1. Location of sampling sites.

***Sampling methods and analysis**.* Based on the sampling sites, the sediment samples were taken by digging the sediment using PVC pipe. The depth of sampling on the sediment was 10 cm. On each sampling site, 3 digging locations were determined and collected, horizontally crossing the river, then all the samples were homogenized into the sampling jar. Thus, the total sediment sample of every sampling site was 1 kg. Samples were collected on June 2022, during the dry season.

Later, the samples were analyzed on the laboratory of Faculty of Civil Engineering and Planning, Islamic University of Indonesia (UII), which adopting NOAA MDP (Marine Debris Program) method, then displayed by diagrams and tables. From this method, the amount, forms, and size/dimension of the microplastics were analyzed by using imaging software cellSens ver. 3.2. The photos of the microplastics were taken by using camera and then analyzed. For identification of the polymer types, FT-IR (Fourier Transform Infrared; Shimadzu IR; OriginPro 2019b 64-bit 9.6.5.169) spectrophotometry test on bulk samples was performed. The bulk samples of each sampling site were divided into 4 quadrants. From those quadrants the types of polymers, size, and forms were analyzed. By the polymer database used on the computer program, the polymer's functional groups were analyzed and matched, thus the polymer types were identified based on the database (LabSolutions IR ver. 2.25) installed which was match on the hitlists.

Results

***Size**, **form**, **and microplastic amount in sediment**.* On 6 sediment samples microplastics were found with various types, size, and form. In all 6 sample sediments fragments, granules, films, and fibers were found. Some of the sample photos were shown on Figure 2.

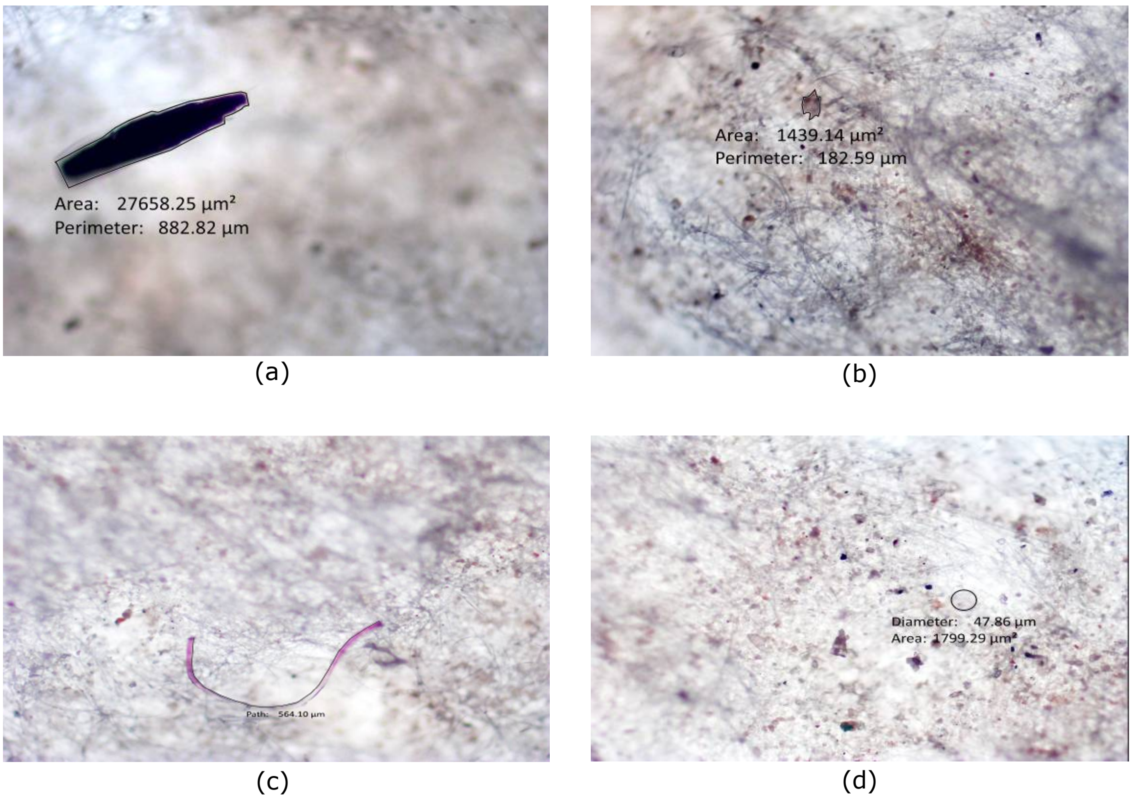

Figure 2. Microplastic types found in sediment: (a) fragment; (b) film; (c) fiber; (d) granule.

The main characteristic of microplastic fragments is their shape in the form of shards of plastic, not like films which are in the form of sheets or fibers. Fragments may be produced from bottles, jars, mica folders and small pieces of PVC pipes. Fragments can be observed clearly under a microscope. Some of the microplastics obtained are fragments of product packaging, for example food packaging. Film is a secondary plastic polymer derived from the fragmentation of plastic bags or plastic packaging and has a low density. Film has a lower density than other types of microplastics, making it easier to transport (Purba 2018).

Fiber is a secondary source with an elongated shape derived from monofilament fragmentation of nets, ropes and synthetic fabrics. Fiber occurances are correlated with higher fishing activities, like using nets, thus it contributes the debris into the seawater. Fiber can also emerge from laundry waste. Granules or pellets are directly produced by the factory as raw materials for any plastic products. Granules are a type of microplastic in the form of regular granules, white or brown in color, dense and about 1 mm in size (Viršek et al 2016; Anik et al 2021).

Microplastic types, amounts, and size. The most common type of microplastic found from 6 sample points in the Code River was fragment, especially at T3 (625 particles kg^{-1} of sediment), as shown in Figure 3. A secondary source of microplastics is in the form of film, as the product of microplastic breakdowns in the aquatic environment. Microplastics from this secondary source are often associated with areas with high population density (Browne et al 2011).

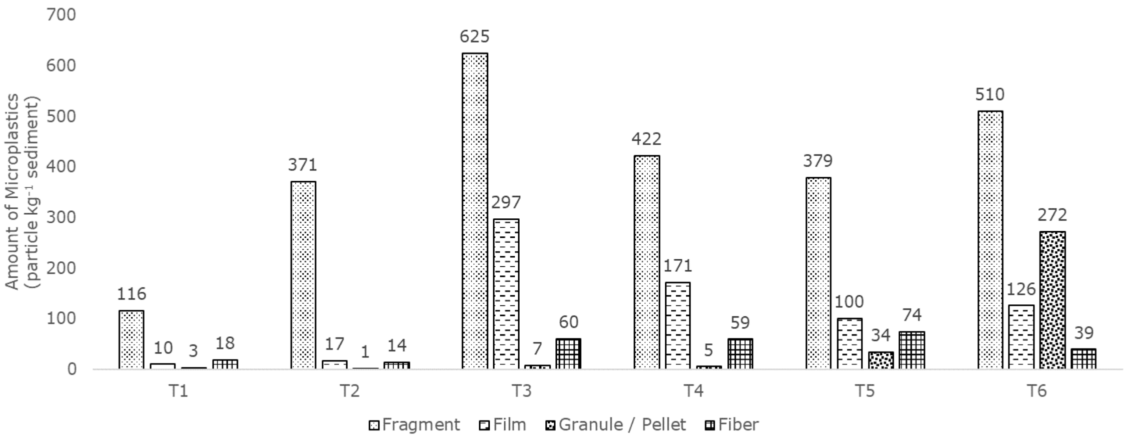

Figure 3. Amount and type of microplastics found on sediment samples.

Granular type microplastics was found the least on all sediment samples, except at T6. At T2 it was found 1 particle kg^{-1} of sediment. As shown on Figure 3, as the river flows to the downstream of the segment, the more number and types of microplastics were found. T1 was situated on the north side of Yogyakarta City. The environment around the sampling sites were covered with greenbelt. It was the opposite on the downstream, since a lot of human activities take place and many buildings were situated nearby the riverbanks. Thus, it contributed to the high number of amount and types of microplastic. Fragments were the most common found in all sampling sites, regardless the sampling site on the Code River segment. At T3-T6 some activities were found side of the riverbanks, like hotels, markets, fishing ponds, cullinary sites, business stores, and residents. Based on the sampling sites, all the microplastics had various size, as shown in Table 2.

Microplastics have different sizes and areas because each region has different levels of pollution and activity. Vegetation and river flow discharge can also affect the size of the microplastics in the sediment. Boucher & Friot (2017) noted that exposure to sunlight (photodegradation), degradation of living things (biodegradation) and thermal degradation or water temperature also contribute to the microplastic formations.

Table 2

Sizes of each microplastic types

Sampling site	Fragment		Films		Granules		Fibers
	Length (μm)	Area (μm^2)	Length (μm)	Area (μm^2)	Diameter (μm)	Area (μm^2)	Length (μm)
T1	118-882	990-27,685	182-1,359	1,439-65,807	47-57	1,799-2,636	92-564
T2	118-1,440	838-42,439	79-119	377-813	51	2,096	124-526
T3	138-548	1,211-18,312	117-1,563	919-70,697	24-48	469-1,865	97-1,264
T4	121-1,012	791-54,113	103-1,091	704-48,910	38-46	1,185-1,715	193-1,502
T5	101-831	556-25,612	77-908	418-43,445	35-61	1,014-2,930	164-910
T6	92-1,185	564-74,551	104-1,383	674-61,467	40-64	1,317-3,307	171-821

Changes in bigger plastic turning into a smaller size due to the degradation can be promoted by sunlight, temperature, hydrolysis, animal and human activities. Degradation caused by sunlight through UV rays and hot temperatures can trigger oxidative degradation of polymers. During the degradation process, plastic waste changes color or discolour and causes the texture of the plastic to become softer and easily crumble over time and turn into microplastic. In addition, animal bites can also cause the presence of microplastics in aquatic environments such as in sediments and also the presence of hydraulic waves and friction that occur in waters. Large plastics can be broken down into small sizes in the form of fragments (GESAMP 2015). Microplastics can disrupt endocrine system due to carcinogenic substances which are accumulated through the biomagnification and bioaccumulation process (Rochman et al 2015). Therefore, this is a concern for the condition of biota because of the adverse effects caused by microplastics when consumed which can cause damage to the digestive system both physically and chemically.

FT-IR results and analysis. FT-IR results were obtained according to the database in the FT-IR software program. We collected a lot of kinds of polymers, which can be divided into 2 different groups: the synthetic polymers and the natural polymers. Based on the results, Table 3 and Table 4 contain the polymers detected by FT-IR analysis. The results were the cumulative number of four quadrants from each sampling site, which matched with the database. Based on the name of the labels, Table 3 and Table 4 contain the cumulative number.

Table 3

Types of synthetic polymers in sediments

Sample code	*Amount of match*					
	Polyacetylene	*Polyacetal*	*Polyethylene terephthalate*	*Polyetherimide*	*Polyamide*	*Polyvinyl chloride*
T1	3					
T2	1	2	2	1		
T3	2	1	1	3	2	
T4	4			1	6	
T5	4					1
T6	5					

Table 4

Types of natural polymers in sediments

Sample code	*Amount of match*		
	Cellulose	*Protein*	*Zein*
T1	18		
T2	27	1	
T3	30	7	1
T4	33	8	
T5	35	9	2
T6	13	9	

Polyacetylene was primarly found in each sampling sites. Some other synthetic polymers were also found like: polyacetal, polyethylene terephthalate (PET), polyetherimide (PEI), polyamide, and polyvinyl chloride (PVC). Meanwhile, on the natural polymers, cellulose and proteins were found on each sampling sites, except at T1, with cellulose dominating the number size. PET is a thermoplastic plastic polymer resin from the polyester group. One of the biggest sources of waste of PET is mineral water bottles (Thachnatharen et al 2021). PEI is commonly used for manufacture of micro, ultra and nanofiltration membranes because of its excellent physical characteristics. In addition, PEI is an amorphous polymer that has a thermal resistance of up to 200°C. It exhibits good electrical properties, stable over a wide range of temperatures and frequencies, and inherently being flame resistant without using any additives. Based on the structure, PEI contains chains of various aromatic heterocyclic and cycloaliphatic groups (Johnson & Burlhis 2007; Borodulin et al 2020).

Polyamide might be detected from the nylon, since nylon contains amide bonds in its monomer structure. There are a lot of nylon types, depending on the types of its monomer, such as: nylon 6-6, nylon 6-9, etc. Nylon has a lot of applications, like ropes, nets, parachutes, tents, raincoats, carpets, and many other materials related with fabrics (Apipah et al 2014; Periyasamy & Tehrani-Bagha 2022). PVC is a very popular and versatile polymer used for construction (pipelines) due to its properties, non-corrosive, and resistant from damage caused by biological sources. PVC also can be combined with plasticizer, thus it can be applied as cable insulator. Because of its properties, PVC is hard to degrade in the environment, yet the potency to recycle it is still high and possible to develop (Lewandowski & Skórczewska 2022).

Some of natural polymers were also detected by FT-IR database match. The majority were from cellulose, protein, and zein. Cellulose in the sediment might come from any parts of plants which are situated nearby the riverbanks, meanwhile protein might come from any degraded animal tissues or products, like wool and silk; or plants , like cotton and linen. Since FT-IR results qualitatively evaluated the types of the polymers, it doesn't indicate the percentage of the microplastic types. Furthermore, the samples were in bulk, it means that a lot of polymers contribute to the aborbance on the FT-IR diagram. Thus, the overlaps were inevitable. The identity of the polymers then was evaluated based on the database and especially on by the fingerprint wavelength number (below 1000 cm^{-1}). As Figure 4 shows, polyacetylene gave absorpsion on 2920 cm^{-1} and 1650 cm^{-1}, yet in this FT-IR spectrum (Quadrant 4, T1) other polymers also contribute to the peak emergence, like O-H spectra (3000-3500 cm^{-1}). This peak may emerge because of the presence of the natural polymer like cellulose which contains hydroxyl functional groups.

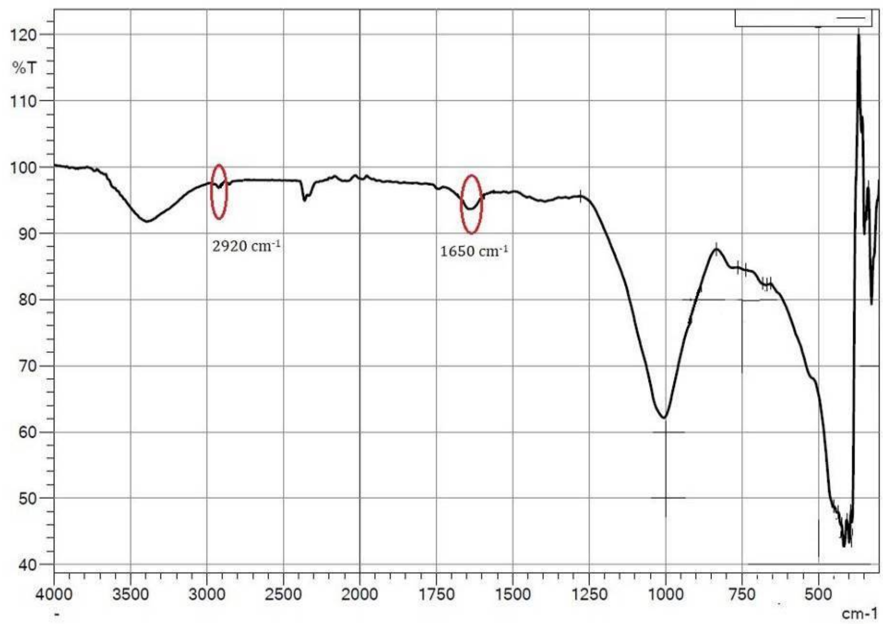

Figure 4. C=C ALKENE & C-H ALKANE Polyacetylene Absorption Wavelength (Sample Code T1, Quadrant 4).

Microplastic dispersion areas. Six sampling sites were grouped into 3 main groups: upstream area (T1 and T2), middle stream (T3 and T4), and downstream (T5 and T6). Microplastic (regardless the forms) were found the largest on the middle stream, 1,646 particle kg^{-1} sediment. Upstream area contained the least microplastic (550 particle kg^{-1} sediment), as shown in Figure 5.

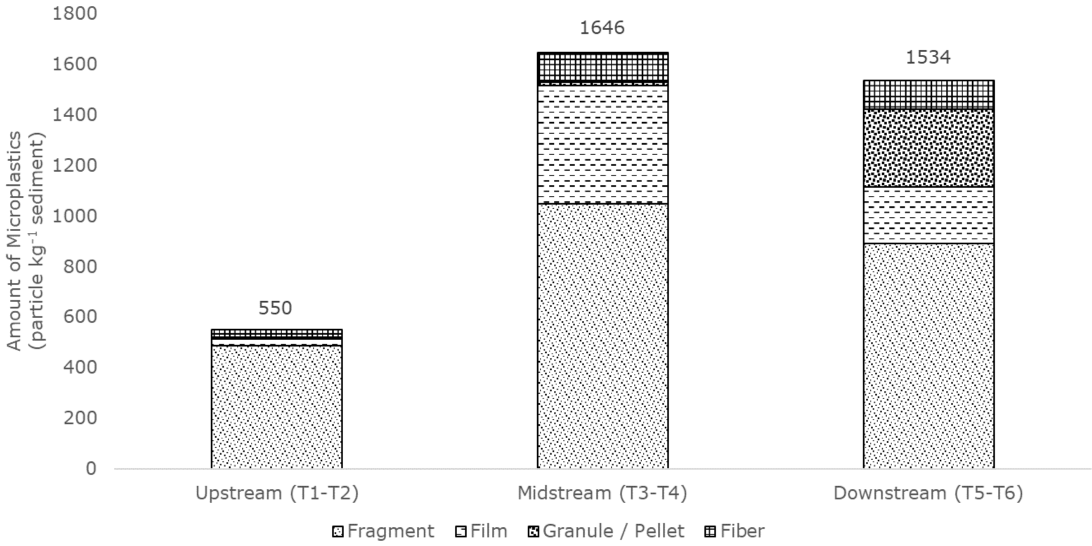

Figure 5. The distribution of microplastics.

Population density has correlation with plastic waste generation on an area (Barnes et al 2009; Willis et al 2017). Several activities around are noticable in the middle stream segment, such as settlements, hotels and culinary tours. It is also very close to the center of tourist attractions such as the Yogyakarta Pal Putih Monument and the Malioboro. The downstream zone has residential, hotel and hospital activities which may cause an abundance of microplastics in sediments. Meanwhile, the upperstream area (T1-T2) has less direct contact to any human activities. Thus, the microplastic found on those areas highly probable come from the higher northern parts of the riverbanks. Moreover, the direct access to the river is not found at T1-T2, contrasting T3-T6 that have direct access to the river. It leads to the plastic waste disposal generation next to the river flow. It means that the chance to generate more microplastic becomes higher, as shown in Figure 6.

(a) (b) (c)

Figure 6. (a) Upstream at T1, (b) Middlestream at T3, (c) Downstream at T6.

Sediment type may also influence the presence of microplastic on the sediment. Microplastic abundance tends to decrease with the larger sediment grain size exponentially (Vermeiren et al 2021). At T1-T2 the sediment on those sampling points have more bigger gravels and pebbles. It is different with T3-T6 which are dominated with smaller gravel and sand. Thus, the microplastics are easily trapped in the sediment. With the bigger gravel size, the microplastics are more easily washed away along the river flow.

Prabowo (2020) had also conducted a study about microplastics on Code River. The sample segments were taken from upstream to the downstream of Code River. Compared with this study, the sampling points of Prabowo (2020) were more diverged, from further upstream near Merapi Mt, down to Bantul Regency; meanwhile this study was conducted especially on the segment of Code River crossing Yogyakarta City. Some samples were concentrated inside or near Yogyakarta City. The data were collected collectively, thus it there was no differentiation between each sampling points. Regardless of the different sampling points, the microplastics in Code River are indicated to increase (Figure 7). Further studies need to be conducted to explore the exposure level of microplastic in Code River.

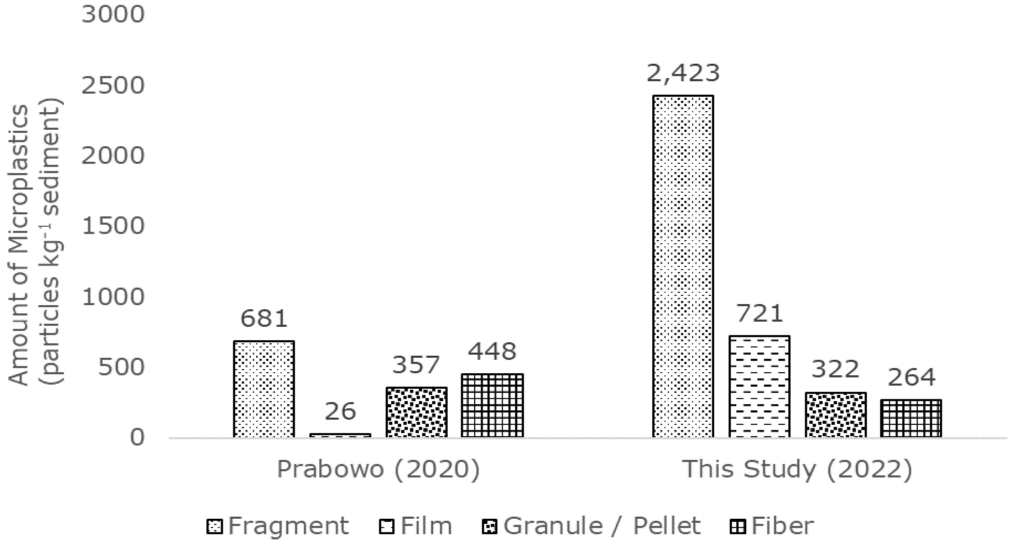

Figure 7. Study results comparison.

Conclusions. Based on the results and analysis, we can conclude that microplastics were found in Code River. All varieties of microplastics (fragment, granule, fiber, and film) were present during the study time. The abundance of microplastics was found bigger at the middle stream of the segment studies, as much as 1,646 particle kg-1 sediment. It also had various size, from the tiniest (granule, 35 μm) to the largest (fragment, 1,440 μm). Compared with previous study, the amount of microplastic in Code River is suspected to be increased, but further studies are needed for investigations.

Conflict of interest. The authors declare that there is no conflict of interest.

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