Effects of surface runoff on the distribution of microplastics in urban rivers

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Abstract

The number of research focusing on microplastics in aquatic environments is exponentially growing. Nevertheless, there is a scarce understanding of the dynamic emissions of these particles into the receiving rivers through surface runoff which represents the biggest non-point source of microplastic pollution. The present study aims to address this gap through a comprehensive assessment of plastic pollution in the primary river network of Kyoto City in Japan. The study involved three main objectives which sequentially clarified the relative role of surface runoff in microplastic pollution of riverine catchments.

Initially, a baseline study was conducted to investigate the occurrence and distribution of plastic debris spanning over a wide array of particle sizes (mesoplastics: 5,000–25,000 µm, large microplastics: 300–5,000 µm, small microplastics (SMPs): 10–300 µm, and microplastic fibers (MPFs): 10–5,000 µm), concurrently in the rivers during dry weather. The concentrations of plastics were moderate compared to the global reports (3,550–15,840 items/m^3; 180–13,180 µg/m^3), and their spatial distribution implied the likely impacts of non-point sources (e.g., surface runoff). The number concentrations increased with decreasing particle size, marking 99.94% of SMPs, including 50% smaller than 40 µm. Conversely, mass concentrations decreased, exhibiting 96% larger than 1,000 µm (64% mesoplastics), along with 2% SMPs. It should be noted that the method used for estimating mass of microplastic particles throughout this study may produce approximately 4 times higher masses than the actual/measured masses, considering the insignificant contribution to the total mass by SMPs. The abundance of MPFs in river water typically surpassed the abundance of microplastic particles of matching sizes under dry weather conditions. This study further highlighted the relevance of employing dedicated analytical procedures like Nile-red staining for MPFs over conventional methods. The river network of Kyoto was found to convey billions of tiny microplastics to the Yodo River, the primary water resource downstream, within a typical dry day.

The second objective aimed to investigate the dynamic emissions of microplastics into the river flow during the real-time occurrence of rainfall and runoff events. This study involved high-frequency sampling of microplastic particles and MPFs in the river throughout three different rainfall events (i.e., light: <2.5 mm/h, moderate: 2.5–7.6 mm/h, and heavy: >7.6 mm/h rainfalls) compared to the previous studies. The event mean

concentrations (EMCs) of particles amounted to 35,000 items/m^3, 929,000 items/m^3, and 331,000 items/m^3; and the corresponding total loads were 0.5 kg, 19.8 kg, and 35.0 kg for light, moderate and heavy rainfalls, respectively. The inter-event total loads of the particles correlate well with the total rainfall, while the concentrations were linked with the number of antecedent dry days. Small-sized particles (10–40 µm) mobilized rapidly at lower rainfall intensities, displaying first flush effects, whereas those over 2,000 µm discharged immediately after the peak rainfall intensity. Overall, the rainfall events increased microplastic loads by 4–110 folds, and EMCs by 10–350 folds compared to the dry weather. This study provided the first evidence that dynamic emissions of microplastics are well-correlated with those of suspended solids, which is beneficial in developing size-targeted interventions for microplastics in surface runoff. Additionally, it revealed a lesser impact of runoff emissions on riverine MPFs compared to microplastic particles, regardless of their comparable dynamics in rivers during runoff events.

The third objective utilizes the data from objectives 1 and 2 to develop a mass balance approach to finally quantify the relative contribution of surface runoff to the annual microplastic discharges of the river catchment compared to the controlled emissions via treated wastewater. The total microplastics (10–5,000 µm) released from the catchment amounted to 269.1 tons/annum (range: 89.2–335.5 tons/annum), of which approximately one-fifth is intercepted and removed by the wastewater treatment plants (WWTPs). On an annual scale, the treated effluent occupies only 0.1% (range: <0.1–0.3%) of the total microplastics released to the river network, while the remaining portion is dominated primarily by surface runoff emissions (average: 98.9%; range: 96.8–99.0%), and trivially by atmospheric depositions in dry days (average:1.0%; range: <1.0–3.0%). We demonstrated that microplastic emissions via unregulated surface runoff may inflict more severe pollution effects than untreated wastewater. Moreover, only 18% of the total year where moderate to heavy rainfalls occur is crucial for controlling microplastic pollution of urban rivers. Overall, this study provided plenty of insights into size-based distributions and emission dynamics of microplastics in urban rivers, which will be beneficial in developing control measures for microplastic pollution of urban catchments, particularly concerning the effects of surface runoff.

Keywords: Microplastic pollution; Spatiotemporal dynamics; Riverine catchments; Synthetic fibers; Urban runoff; Wastewater treatment

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CHAPTER 1. Introduction

1.1 Background and rationale

The mass production of plastics commenced in the 1950s and reached 390.7 million tons by the end of 2021 (Plastic Europe, 2022). Subsequently, over 6,300 million metric tons of plastic waste has been generated worldwide as of 2015, of which ~80% is accumulated in landfills or the natural environment (Geyer et al., 2017; Plastic Europe, 2022). Once introduced into the environment, plastic debris may disintegrate into smaller fragments that are generally termed "microplastics", due to numerous physical, chemical, and biological processes (Andrady, 2015; Ter Halle et al., 2016; Zbyszewski et al., 2014; Zettler et al., 2013). While microplastics are regarded as plastic particles spanning within the size range of 1 µm to 5 mm (Frias et al., 2019), much smaller and larger particles are categorized as nanoplastics (<1 µm), mesoplastics (5–25 mm), and macroplastics (>25 mm) (Andrady, 2015; Horton et al., 2017). Although the current knowledge is mostly concentrated on the "microplastic" fraction, exploring the occurrence of plastic debris on a continuous size scale of particles that extend beyond the micron size is thought to be crucial for understanding the drivers and fate of (micro)plastic pollution (Horton et al., 2017).

Microplastics have gained the attention of researchers due to their ubiquity and persistence in terrestrial and aquatic environments and are regarded as emerging contaminants considering their ecotoxicological risks (Prokić et al., 2019). In aquatic environments, these particles can be readily taken up by organisms due to their miniature size, and bioaccumulate and bio-magnify through food chains (Cole et al., 2011). Furthermore, they may inflict physical damage and toxicological effects on biological lives (Rebelein et al., 2021; Ziajahromi, Kumar, et al., 2017), and act as a carrier of micropollutants (Bakir et al., 2016; Cole et al., 2011). Although exposure via ingestion and inhalation can be a concern, the human health effects of microplastics remain largely unknown (Akdogan et al., 2019).

These tiny particles may occur in different morphologies and types (e.g., fibers, fragments, spheres, and films) in various environmental matrices depending on their sources of origin. Urban centers represent the hotspots of microplastic pollution owing to the intensive anthropogenic activities involved (Yonkos et al., 2014). Subsequently, urban

rivers act as receptors and sinks, as well as major pathways of those microplastics in the global oceans (Lebreton et al., 2017), where mismanaged plastic waste occupies 80–85% of marine litter (Auta et al., 2017). The research to date has revealed plenty of knowledge on the abundance, characteristics, occurrence, spatiotemporal distribution patterns, and implications of microplastics in riverine urban clusters worldwide by investigating a multitude of environmental media (e.g., water, sediments, biota, and air) and sources (e.g., wastewater, sewage sludge, surface runoff) of microplastics (Browne et al., 2011; Eo et al., 2019; Kataoka et al., 2019; Leslie et al., 2017; Murphy et al., 2016; Piñon-Colin et al., 2020). Nevertheless, a lot of details remain unrevealed with regard to microplastic pollution of Japanese riverine environments that represent important pathways of plastic waste in the North Pacific Ocean and the adjoining maritime zones. Moreover, there is a dearth of knowledge on microplastic emissions propagated by rainfall and subsequent runoff events on a global scale, although they are regarded as the key moments of microplastic pollution in aquatic environments (Hitchcock, 2020).

Furthermore, the sources of microplastic in urban rivers are broadly categorized as point sources and non-point sources (Kataoka et al., 2019). Wastewater treatment plants (WWTPs) are identified as the critical point sources of microplastics in urban catchments, facilitating easy monitoring and controlling of microplastic emissions (Browne et al., 2011; Murphy et al., 2016). On the contrary, the emissions via non-point sources, mainly stormwater runoff are dispersed over a wide area, and thus, are difficult to regulate (Cho et al., 2023; Piñon-Colin et al., 2020). It is imperative to distinguish between the proportions of microplastics disseminated from these sources in order to derive appropriate interventions for microplastic pollution at the catchment scale. A few studies to date have attempted to distinguish the relative contribution of these sources to the annual microplastic emissions of urban catchments (Bailey et al., 2021; Chen et al., 2022; Schernewski et al., 2021). However, most of them either involved combined sewer systems that cause the mixing of stormwater and wastewater, or considered insufficient sampling performed at poor time resolutions to capture the real-time dynamics of microplastic emissions during rain and to represent the annual rainfall patterns of the respective region. Moreover, the existing studies provide scarce information on particle-size-specific emission characteristics of microplastics although the treatment measures for microplastics in surface runoff may highly rely on particle size.

1.2 Objectives

The ultimate goal of this study was to clarify the contribution of surface runoff to the microplastic pollution of urban rivers using field data obtained from a typical urban riverine catchment in Japan. The primary river network in the metropolitan Kyoto City in Japan, comprising its two major rivers, Katsura and Kamo was selected as the study area of this research as it depicts a perfect fit for an urbanized watershed. The aforementioned end goal was achieved through the specific objectives listed below.

1. To investigate the occurrence and distribution of plastics particles (10–25,000 µm) and microplastic fibers (10–5,000 µm) spanning over a wide size range in an urban river network in Japan during dry weather.
2. To elucidate the dynamic emissions of microplastic particles and fibers (10–5,000 µm) into an urban river during the occurrence of rainfall and runoff events of different characteristics, and to compare those wet weather data with the respective dry weather data to elucidate the runoff-driven changes to the microplastic profile of the river.
3. To quantify the relative contributions of surface runoff (uncontrolled emissions) and treated wastewater effluent (controlled emissions) to the annual discharges of microplastics (10–5,000 µm) from an urban catchment using a mass balance approach.

1.3 Thesis outline

Chapter 1 Introduction

The first chapter discusses the background of this dissertation, highlighting the motivation and the rationale for performing the present study. Furthermore, the key objectives of the study are explained, and the way in which the dissertation is structured to achieve those objectives is described.

Chapter 2 Literature review

This chapter reviews the background knowledge of microplastics and identifies the gaps in existing research focusing on the effects of surface runoff on the distribution of microplastics in urban rivers.

Chapter 3 Occurrence and distribution of plastic particles (10–25,000 μm) and microplastic fibers in the surface water of an urban river network in Japan

The work described here reports the magnitude, characteristics, and spatial distribution patterns of plastic pollution in a typical urban river network in Japan under dry weather conditions by investigating plastic debris spanning over a wide size range, including mesoplastics (5–25 mm), and microplastic particles and fibers (10 μm – 5 mm). These data are compared with those from previous reports from similar study environments within Japan and other parts of the world to clarify the contribution of Japan to the global emissions of riverine plastics.

Chapter 4 Inter-event and intra-event dynamics of microplastic emissions in an urban river during rainfall episodes

This chapter discusses the effects of rainfall characteristics on the inter-event and intra-event dynamics of various size clusters of microplastic (particles and fibers spanning between 10 μm – 5 mm) emissions; rainfall-induced changes in the abundances and

characteristics of microplastics with respect to the dry weather (based on the data from Chapter 3); and the implications for microplastic pollution control of rivers based on the present findings.

Chapter 5 A mass balance approach to quantify annual microplastic emissions of urban catchments: surface runoff *vs* wastewater sources

Chapter 5 combines the data from Chapters 3 and 4 to quantify the annual microplastic stocks (10 µm – 5 mm) being discharged to an urban river from its respective catchment, using a mass-balance approach. More importantly, it clarifies the relative contribution of controlled/managed sources (e.g., treated wastewater effluent) and uncontrolled/unmanaged sources (e.g., surface runoff) to the annual microplastic emissions of a well-developed urban catchment; and further discusses the potential interventions for microplastic pollution of urban clusters in both developed and developing regions based on the present learnings.

Chapter 6 The final chapter recaps the key findings of Chapters 3, 4, and 5, indicating the accomplishment of the three main objectives of the study. Moreover, the overall conclusions and the new findings of the dissertation are highlighted along with the recommendations for future research.

CHAPTER 2. Literature Review

2.1 Plastics and microplastics

The discovery of Bakelite in 1907 marked a revolutionary moment in modern human lives, by opening gates to the mass production of various polymers and plastic formulations (Shashoua, 2012). Plastics are produced by polymerization of monomers derived from oil or gas, and generally processed with a range of chemical additives to make them fit for use (Thompson et al., 2009). The uses of plastics range from food packaging to medical and technological applications, owing to their versatile characteristics including lightweight, low thermal and electric conductivity, resistance to corrosion, low cost, and durability (Frias et al., 2019). As of 2021, the global mass production of plastics reached 390.7 million tons per annum compared to the first statistics of 1.5 million tons in the 1950s (Plastic Europe, 2022). Consequently, the handling of plastic waste has become challenging ascribing to their low degradability. Despite the recycling efforts, an enormous amount of plastic waste is mismanaged and ends up in landfills, exacerbating environmental pollution (Geyer et al., 2017).

The concerns of plastic pollution were raised when plastics were found in the global oceans, accumulating an estimated 10% of the plastics that have been produced globally (Avio et al., 2017). The large plastic debris that are commonly known as “macro-plastics” cause numerous problems including, aesthetic issues, interference with marine industries such as shipping and aquaculture, entanglement and ingestion by marine birds, and mobilization of alien marine species (Cole et al., 2011). These begin to slowly degrade with exposure to physicochemical and biological processes in the natural environment (e.g., mechanical abrasion, photodegradation, hydrolysis, thermal oxidation, chemical oxidation, and biodegradation), leading to small fragments of increasing environmental concern that are commonly known as “microplastics” (Andrady, 2015).

The term “microplastics” was initially presented by Thompson et al. (2004) with the identification of small plastic debris in the sediments and waters of Europe. Later, Arthur et al. (2009) suggested an upper size limit of 5 mm for microplastics. A more detailed definition was introduced by Cole et al. (2011) based on the origin of plastic debris, as primary and secondary microplastics. Typically, primary microplastics are intentionally manufactured plastic granules of micron size, that are widely used in

personal care products, industrial abrasives for delicate surfaces, cleaning agents, coatings and paints, drilling fluids in the oil and gas industry, and as original resins and pellets for the manufacture of finished plastic products (Hale et al., 2020). Additionally, microplastic fibers that shed from clothing and other textiles like fishing nets are also considered a form of primary plastics (National Geographic Society, 2023). The secondary microplastics are derived from the breakdown of macroplastics (as described above) and are far more abundant than primary microplastics (Hale et al., 2020).

The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) suggested that "*Microplastics are plastic particles <5 mm in diameter, including the particles in the nano-range (1 nm*)" (GESAMP, 2016). Although the opinions remain widely divided on an appropriate nomenclature, plastic particles smaller than 1 *μm* are generally recognized as "nanoplastics", and microplastics are largely considered a transitionary state between macroplastics (consisting of mesoplastics in the size range 5–25 mm) and nanoplastics (Figure 2-1) (Hale et al., 2020). A consensus and all-inclusive clarification for microplastics was recently proposed by Frias et al. (2019), such that *"Microplastics are any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 μm to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water".*

2.2 Sources, pathways, and implications of microplastics in rivers

2.2.1 Role of rivers in global microplastic pollution

The attention on microplastics was predominantly raised as the massive "garbage patches" in the world's great oceanic gyres were unveiled (Hale et al., 2020). The abundance of microplastic debris in the global marine environments has been estimated at 12–125 trillion particles (Lindeque et al., 2020), symbolizing them as the ultimate sinks of microplastics (Akdogan et al., 2019). As of today, microplastics have been detected in various environmental media, including in the waters and sediments in aquatic environments, soil, air, and biota, and even in the most pristine locations on earth exhibiting the ubiquity of microplastic pollution.

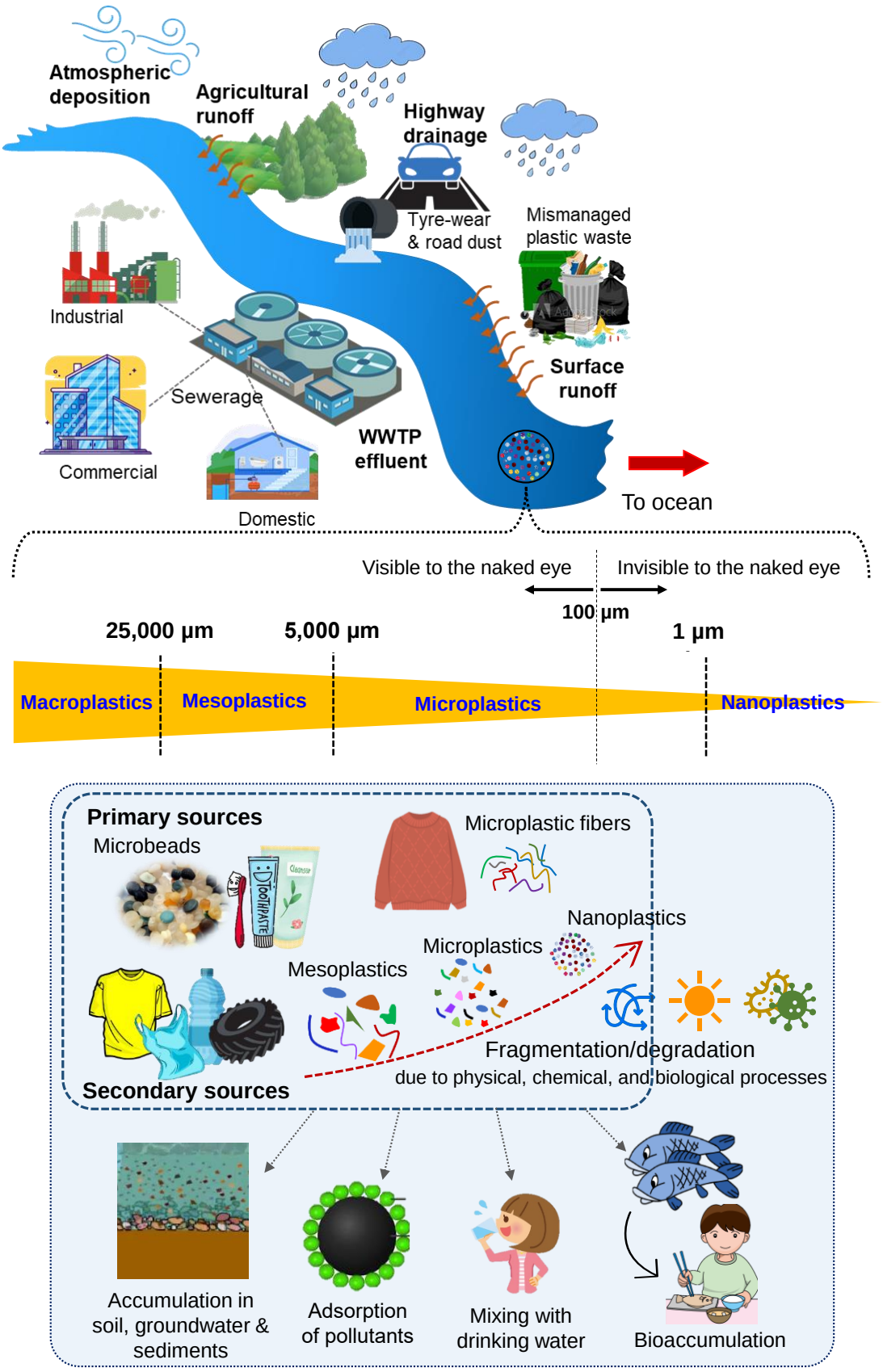


Figure 2-1 Size classification of plastic debris and their sources and pathways in rivers

Riverine systems represent a critical element of the hydrosphere and biosphere that fosters ecological diversity (Bai et al., 2022). While global oceans are known as the ultimate sinks of land-sourced microplastics, rivers are described as the primary conduits for the plastic litter in the oceans (Meijer et al., 2021). However, the abundance of microplastics is found to be relatively high in these river compartments compared to the marine environments, because of their closer proximity to urban centers where plastics are produced, consumed, and disposed of (Yonkos et al., 2014). Additionally, population density, urban ratios, and mismanaged plastic waste generation are found to be correlated with the abundance of microplastics in rivers (Kataoka et al., 2019).

A model-based study by Meijer et al. (2021) revealed that 1000 rivers across the globe transport 0.8−2.7 million metric tons of plastic litter to the oceans annually, accounting for 80% of the total annual emissions. In particular, the urban rivers from Southeast Asian and West African regions are found to be the hot spots of these plastic emissions, and the highest pollution levels are reported in the rivers from the Philippines (3.6×10^5 tons/year) > India (1.3×10^5 tons/year) > Malaysia (7.3×10^4 tons/year) > China (7.1×10^4 tons/year) > Indonesia (5.6×10^4 tons/year) (Meijer et al. 2021). Plenty of observational studies conducted at the regional scale have also confirmed that urban river basins are major sources that export microplastics to the oceans.

In addition to being a central transportation medium for microplastics, the complex hydrodynamics of rivers may result in the accumulation, retention, and remobilization of microplastics over varying spatial and temporal scales as well (Kumar et al., 2021). As a result, microplastics generated from numerous sources have been detected in widely varying abundances in the surface water and sediments of rivers. Microplastics generated from various sources reach the riverine environments through wastewater effluents and sludge applications, combined sewer overflows, surface runoff, and atmospheric transmissions. These are broadly categorized as point sources and non-point sources, which will be further elaborated in Section 2.5. WWTPs have been widely investigated as key point sources as well as sinks of microplastics which retain over 90% of the microplastics carried along with the influent (W. Liu et al., 2021). However, a majority of the WWTPs worldwide utilize combined sewer systems to convey both sewage and stormwater, which results in direct releases of microplastics into the receiving waters through combined sewer overflows (CSOs) during the occurrence of heavy rainfall events. Additionally, WWTPs perform poorly in removing very small microplastics and

microplastic fibers, and freely discharge them to the natural waters along with the treated effluents. On the other hand, the United Nations reported that only 20% of the wastewater generated worldwide is being disposed of through WWTPs (Waldschläger et al., 2020), hence untreated wastewater remains a crucial source of microplastics in river systems globally.

In addition to wastewater discharges, the sewage sludge produced by WWTPs also represents a significant source of microplastics (especially microplastic fibers), owing to its wide application as a fertilizer in agriculture, disposal in landfills, and incineration (Nizzetto, Futter, et al., 2016). These microplastics may consequently leach into the ground, contaminating groundwater and soil. Along with accumulations on impermeable surfaces, MPs may also mobilize into freshwater environments through surface runoff and atmospheric transmissions (Allen et al., 2019; Dris et al., 2018; Piñon-Colin et al., 2020).

2.2.2 Implications of microplastics

Microplastics are known to impose detrimental physical and chemical hazards on freshwater biota. The physical interactions are often encountered through ingestion. Due to their small size, microplastics are easily bioavailable to organisms and subsequently bioaccumulate through food chains (Cole et al., 2013; Lusher et al., 2015). Ingestion of microplastics has been reported to cause ecotoxicological effects in aquatic biota, including digestive and gastrointestinal blockage, oxidative stress, damage to organs, and even death (Franzellitti et al., 2019; Parrish et al., 2019). Especially, microplastic fibers are found to be frequently ingested and entangled by aquatic organisms owing to their high length-to-diameter ratio (Dris et al., 2018).

The chemical hazards of microplastics are due to the leaching additives/plasticizers and the toxic organic and inorganic contaminants, and other persistent organic pollutants that are adsorbed to the large surface area of microplastics (Cole et al., 2011; W. Wang et al., 2017). Additionally, microplastics may also act as a vector for pathogens that form biofilms on the surface of microplastics (Parrish et al., 2019). The toxicological effects comprise changes in gene expression, endocrine disruption, cellular stress, tissue damage, delayed reproduction, improper development, impaired metabolism and respiration, behavioral changes, and increased mortality

(Ogonowski et al., 2016; Von Moos et al., 2012; Kumar, et al., 2021).

The risks of microplastics to human lives have still not been properly understood. Nevertheless, the potential exposure through ingestion (via food and drinking water) and inhalation is suspected (Koelmans et al., 2019). Additionally, indirect impacts on human lives could be caused by economic and ecosystem service losses (Wilcox et al., 2015).

2.3 Methods of sampling, extraction, and analysis of microplastics in riverine environments

The methodologies and analytical techniques employed in the detection of microplastics in rivers are derived from freshwater studies, which in turn originated from the early studies on marine microplastics (Eriksen et al., 2013). The comparability of the results of different studies reporting microplastic data from similar water environments is challenging, owing to the disparities between the protocols followed, in the absence of standard methodologies (Kumar et al., 2021). This section summarizes and compares some of the most commonly used methods in sampling, processing, and analysis of riverine microplastics (Figure 2-2).

2.3.1 Sampling of microplastics

Sampling of microplastics is typically carried out in two ways: bulk water sampling and volume-reduced sampling (Dris et al., 2015; Irfan et al., 2020; Mani et al., 2015) (Figure 2-2). Bulk water sampling refers to collecting the water sample as a whole using a container, and transferring it to the laboratory for further processing, whereas the volume-reduced method refers to the recovery of solid matrices in the water sample using in-situ filtration (using sieves or nets) (Hidalgo-Ruz et al., 2012). The latter is usually performed with manta nets or trawl neuston nets, conical driftnets, plankton nets and microplastic traps of different mesh sizes, or filtration devices with stacked sieves (Dris et al., 2018; Lahens et al., 2018; Lechner et al., 2014; Moore et al., 2011).

Bulk water sampling is easy to perform and quick but the volume of water that can be sampled at a time is limited (0.25 to 20 L). The low sample volumes will be sufficient for the analysis of small microplastics, but hardly provide representative samples for larger plastics which are found at lower abundances compared to small particles (H. C. Lu et al., 2021). Volume-reduced sampling on the other hand is time-

consuming, and laborious but permits a representative sample through filtration of a bigger volume of water (5 L to 310 m^3). Nevertheless, the lower size limit of particles that can be analyzed with this method is restricted to several hundreds of micrometers, due to quick clogging of the filters/nets. Bulk water sampling on the contrary adopts a stepwise filtration process and thus recovers much smaller particles (<10 μm) through reduced clogging (Barrows et al., 2017).

2.3.2 Pre-treatment of microplastics

Upon sampling, it is necessary to process the samples to extract the potential plastics for further analysis. While the extraction methods would be matrix-specific, they typically involve two key steps, viz. chemical or enzymatic digestion and density separation. Chemical or enzymatic digestion is employed to remove the organic matrices in the samples for improved accuracy of the analytical procedures, whereas density separation is performed to eliminate inorganic particles (Figure 2-2).

Past studies have reported three ways of performing chemical digestion; oxidative, acidic and alkaline digestion (Prata et al., 2019), out of which oxidative digestion using hydrogen peroxide (H_2O_2) is the most frequently used method (Jiang et al., 2019). Since digestion using 30% H_2O_2 can be time-consuming, the solution is heated at a controlled temperature (preferably less than 60 °C) over a certain period to expedite the process (H. C. Lu et al., 2021). Additionally, the peroxide treatment can be coupled with Fe(II) solution as a catalyst, to accelerate the rate of reaction of the digestion process (Hurley et al., 2018). This process is known as “wet oxidation”. While it is effective and beneficial, caution should be taken as this process is exothermic. Chemical digestion using acidic and alkaline solutions involves sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl) and nitric acid (HNO_3). While these may not provide sufficient removal efficiency, they may also degrade certain polymer types of plastics (Hurley et al., 2018). On the contrary, digestion with enzymes (e.g., chitinase and lipase) is shown to be effective, yet their usage is limited due to the high costs involved (Yang et al., 2021).

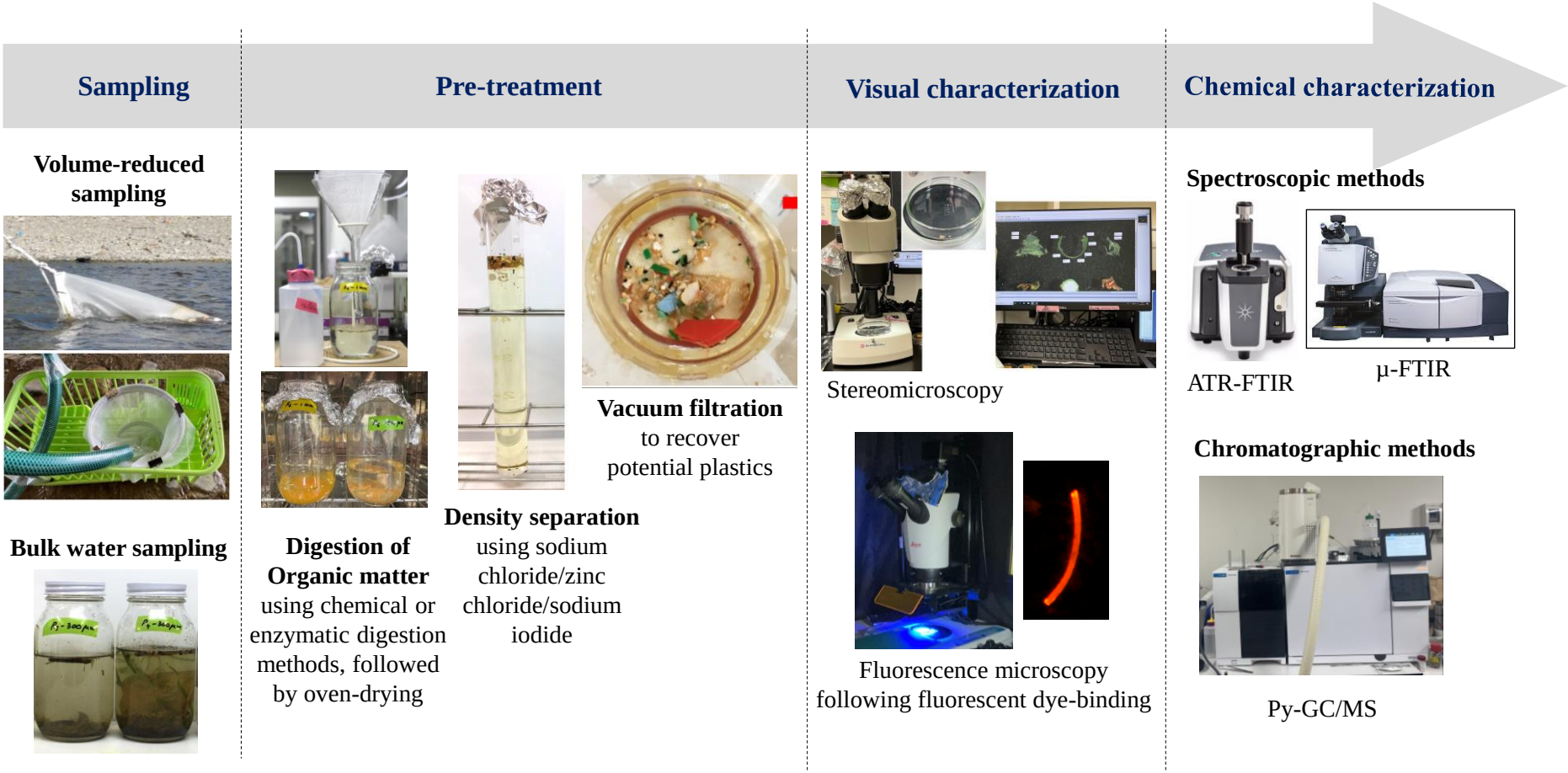


Figure 2-2 Stepwise procedures used in the analysis of microplastics
("ATR-FTIR" refers to attenuated total reflectance fourier-transform infrared spectroscopy, and "Py-GC/MS refers" to pyrolysis gas chromatography coupled with mass spectrometry)

The density separation allows the recovery of microplastics from higher-density particles of non-plastic origin with the use of a high-density salt such as Sodium chloride (NaCl; 1.2 g/cm^3), zinc chloride ($ZnCl_2$; 1.5–1.7 g/cm^3) and sodium iodide (NaI; 1.6–1.8 g/cm^3) (Yang et al., 2021). NaCl is commonly used for this as it is cost-effective, widely available, and non-hazardous. However, it is found to be less effective in extracting denser microplastic polymers such as polyvinyl chloride (PVC) and polyethylene terephthalate (PET), due to its low density. While $ZnCl_2$ and NaI are recognized as better alternatives, their usage is limited owing to the high costs and the toxicity involved (Li et al., 2018). Therefore, mixing with low-density solutions like NaCl and reusing (after recycling) is advised. Moreover, some studies utilized low-density solutions like NaCl for the primary extraction of microplastics before using NaI or $ZnCl_2$ for improved extraction of high-density plastics (Hurley et al., 2018). Density separation is usually repeated several times (up to 5 times) for effective extraction of microplastics in the environmental samples.

At the end of the chemical digestion and density separation processes (they can be performed interchangeably), the samples are vacuum-filtered to separate potential plastic particles from the liquid phase. Filters with mesh sizes less than 20 µm (e.g., Glass fiber filters, stainless steel, cellulose filters, nylon filters, polycarbonate filters and anodisc filters) are commonly used for this (H. C. Lu et al., 2021).

2.3.3 Detection of microplastics (analytical methods)

The most common approach for detecting microplastics is the initial visual screening for identifying potential microplastics, followed by chemical characterization using an appropriate analytical instrument.

2.3.3.1 Visual techniques (non-instrumental)

Visual and non-instrumental techniques Estimating the abundance of microplastics and visual sorting are performed with a microscope (Figure 2-2). This relies on the shape and color of particles, hence the following standardized criteria are adopted to minimize the occurrence of false positives/negatives (Hidalgo-Ruz et al., 2012; Prata et al., 2019).

1. Based on the shape, microplastic particles are roughly divided into five categories: fiber, pellet, foam, film, and fragment.

2. The thickness of microplastic fibers should be homogeneous, and not be tapered towards the ends.
3. A particle (microplastic) should be of uniform color, and if appears in white or transparent, it should be examined under high magnification, and with fluorescence microscopy.
4. Any cellular or organic structure should not be visible along with the microplastic particle.

While microscope (e.g., stereomicroscope, fluorescence microscope, and electron microscope) is the most up-front option in the manual counting and identification of microplastics, they are not effective in detecting particles smaller than 100 μm, and the chance for false positives increases as the size of microplastics decreases (Yang et al., 2021).

Other non-instrumental methods involve hot needle test and dye-binding. In the hot-needle test, the potential plastic particle is brought into contact with a heated stainless-steel needle to confirm its plastic origin (Leads et al., 2019). Dye-binding method refers to fluorescent labeling of potential plastic debris with an appropriate solution such as Nile Red (the most commonly used method) (Shim et al., 2016). The hydrophobic properties of plastics allow them to be fluorescently labeled with a lipophilic solution like Nile Red. Afterward, the stained samples are observed for microplastics through blue or green light under fluorescence microscopy (Shim et al., 2016). Overall, microscopic identification, hot-needle test, and dye-binding do not provide information about the chemical properties of plastics.

2.3.3.2 Polymer identification methods (instrumental)

The common techniques for detecting the polymer characteristics comprise spectroscopy and chromatography (Figure 2-2), out of which spectroscopic methods are extensively used in ~80% of the published research on freshwater microplastics (H. C. Lu et al., 2021). Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy are the most established methods in this category (Besseling et al., 2015), with a few studies utilizing scanning electron microscope (SEM) combined with energy dispersive X-ray spectroscopy (SEM-EDS). Improved FTIR imaging using focal plane array (FPA), and laser direct infrared spectroscopy (LDIR) are among the novel spectrometric techniques reported in the recent studies.

Table 2-1 Pros and cons of various polymer identification methods of microplastics

Analytical method	Pros	Cons
Spectroscopy		
Attenuated total reflectance fourier-transform infrared spectroscopy (ATR-FTIR) and μ-FTIR	• Non-destructive analysis • Well-established and reliable • Ability to analyze a wide size range of particles using different modes (>300 μm using ATR-FTIR; down to 20 μm using μ-FTIR)	• Expensive instrumentation • Labor intensive • Time consuming • Damage of samples due to contact analysis in ATR • Interference to analysis from physical properties of particles, biofilms, weathering, and the presence of water
Focal plane array (FPA)-FTIR and Laser direct infrared spectroscopy (LDIR)	• Automated imaging • Faster analysis of a full filter surface within a limited time. • No interference with filter membranes and impurities	• Expensive instrumentation • Careful sample preparation
Raman spectroscopy	• Non-destructive and non-contact methods of analysis • Well-established and reliable • High-resolution spectra • Ability to identify MPs as small as a few μm • Less affected by the morphology of particles • Does not affect due to the presence of water	• Expensive instrumentation • Labor intensive • Relatively slow performance compared to FTIR • Interference by additives and pigment chemicals in MPs, hence proper sample preparation is crucial
Scanning electron microscope combined with energy dispersive X-ray spectroscopy (SEM-EDS)	• Provides high-resolution images of the surface of plastic particles • Provides details of the elemental composition of plastics, together with the inorganic additives on the MP surface	• Expensive instrumentation • Time-consuming • Exhaustive sample preparation and analysis • Not appropriate for routine analysis of many samples.
Chromatography		
Pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS)	• Reliable • Provides mass-based information • Provides information on polymer types and additive chemicals • Does not require sample preparation	• Destructive analysis • A small amount of samples can be analyzed per run • Does not provide information on particle number, size, shape, and color • Complexity of data
Liquid chromatography coupled with tandem mass spectrometry (LC/MS)	• High recoveries • Provides mass-based information	• Destructive analysis • A small amount of samples can be analyzed per run • Does not provide information on size and physical properties of MPs • Only specific polymer types can be analyzed

These methods detect plastics by comparing the characteristic spectra of a given particle against the reference spectral libraries. On the other hand, chromatographic techniques followed in freshwater-MP studies involved pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) and liquid chromatography coupled with tandem mass spectrometry (LC-MS) (Yang et al., 2021). The pros and cons of each of these polymer identification methods are compared in Table 2-1.

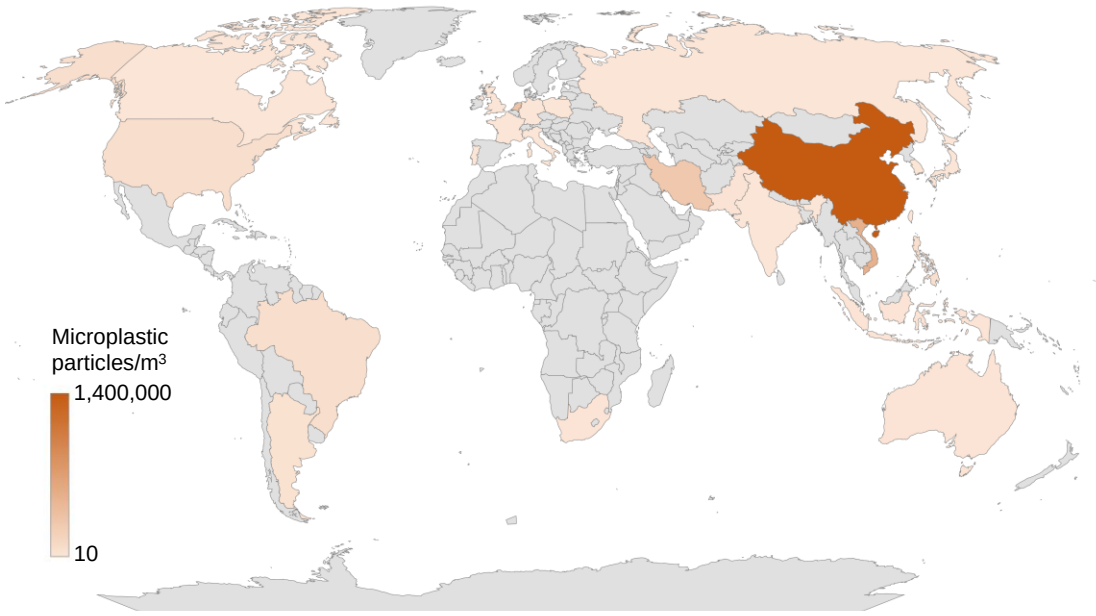
2.4 Characteristics of microplastic pollution in urban rivers

Riverine ecosystems are recognized as sinks as well as conduits for microplastics through their roles of accumulating microplastics in the sediments and transporting microplastics to marine environments along the river flow (Lebreton et al., 2017; Meijer et al., 2021). While both roles contribute significantly to the microplastic pollution of the aquatic environments globally, this section mainly focus on the abundances and characteristics of microplastics detected in the water phase of the rivers, considering the relevance to the main study.

2.4.1 Abundance of microplastics in global rivers

The abundance (concentrations) of microplastics reported from different river systems across the globe are indicated in Figure 2-3. Considering the size-dependability of the abundances of microplastics, this comparison involves only the studies that analyzed particles down to sizes smaller than 300 μm (while the upper limit was set at 5,000 μm). Overall, the concentrations of microplastics in the water column of rivers ranged over five orders of magnitude from 9.20 items/m^3 to 1.39×10^6 items/m^3 with Spain and China indicating the lowest and the highest levels, respectively. Out of the top ten rivers depicting the highest microplastic levels, six belonged to Asia (China > Vietnam > Iran > Philippines > Pakistan > Indonesia), confirming the previous evidence that global plastic pollution of aquatic environments predominantly originated in the Asian region. Most of these countries (including South Africa and Brazil) possess developing economies where plastic waste mismanagement is high (Jambeck et al., 2015).The lowest microplastic levels in river water were noted in European countries like Italy, Germany, the United Kingdom, and France, clearly reflecting the outcomes of satisfactory plastic waste management practices compared to Asian and African regions.

A few studies (not indicated in Figure 2-3) analyzed microplastic fibers as an individual fraction of microplastics, considering their higher existence and contrasting environmental behavior compared to microplastic particles. While microplastic fibers are found to be pervasive in river sediments, the studies on the water phase have also shown concentrations up to 567,000 items/m^3 globally (Kumar et al., 2021), with an average of 985 items/m^3 in the Hudson River, USA (R. Z. Miller et al., 2017), 4–108 items/m^3 in Sein River, France (Dris et al., 2018), and 519,000 items/m^3 in Saigon River, Vietnam (Lahens et al., 2018).



** Size range of microplastics: 20–5,000 µm*
** Only the studies that included particles smaller than 300 µm (as the minimum particle size) are included here*

Figure 2-3 Level of microplastic contamination in the rivers across the globe

(References: Alam et al., 2019; Amrutha and Warrier, 2020; Apetogbor et al., 2023; Barrows et al., 2018; Campanale et al., 2020; Dris et al., 2015; Eo et al., 2019; Han et al., 2020Irfan et al., 2020; Kameda et al, 2021; Lahens et al., 2018; Mani et al., 2019; Mughini-Gras et al., 2021; Osorio, 2021; Pozdnyakov et al., 2020; Rico et al., 2023; Rodrigues et al., 2018; Rowley et al., 2020; Sekudewicz et al., 2021; Tien et al., 2020; Vermaire et al., 2017)

Figure 2-3 illustrates relatively high microplastic concentrations for rivers from some well-developed countries like the Netherlands (Mughini-Gras et al., 2021), and the USA (Barrows et al., 2018), regardless of the lower plastic pollution levels maintained. However, some other studies have testified relatively lower concentrations for these regions, signifying considerable differences between the studies that utilized different

methodologies (Dutch rivers by Mintenig et al. (2020): 11,532 items/m^3; rivers in Illinois, USA by McCormick et al. (2016): 11–5,405 items/m^3). At the same time, various factors such as land use patterns, population density, existence of industries, rates of plastic production, usage and wastage, proximity of the sampling location to the dominant sources of microplastics (e.g., wastewater treatment plants and stormwater outlets), and temporal effects such as occurrence of rainfall may also result in such differences (Wagner et al., 2019).

2.4.2 Variation in size of riverine microplastics.

In the absence of a well-established lower size limit for the detection of microplastics, the existing studies on riverine microplastic considered varying lower size limits that are typically defined by the pore size of plankton nets or filters used in sampling and extraction of microplastics (Frias et al., 2019; Prata et al., 2019). However, it is important to appropriately define the lower size limit of plastics being analyzed, the abundance of plastic debris may widely vary upon the faction of small particles involved. As shown in Figure 2-4, the lower the minimum particle size of microplastics considered, the higher the concentrations obtained for river water. In other words, higher microplastic concentrations were derived from finer pore sizes of nets/filters. For instance, Dris et al. (2015) recovered 30 times higher microplastic abundances with 100 μm mesh-sized net compared to a 330 μm mesh.

Figure 2-4 depicts that when the minimum particle size (lower size limit) reduces by 3 orders of magnitude, the abundance increases by 6 orders. In agreement, Cózar et al. (2014) also established that the concentrations of plastic particles decrease with increasing size, exhibiting a power-law relation. This is due to the continuous fragmentation of larger plastics into a multiplying number of smaller particles due to environmental weathering (Andrady, 2015). It is also evident from Fig. 2 that the number of studies focused on mesoplastics (>5,000 μm), and microplastics smaller than 20 μm are relatively less. This is likely due to sophisticated analytical methods involved in the analysis of smaller microplastics (also nanoplastics), and the exhaustive sampling methods involved with mesoplastics (e.g., large volumes of river water need to be filtered).

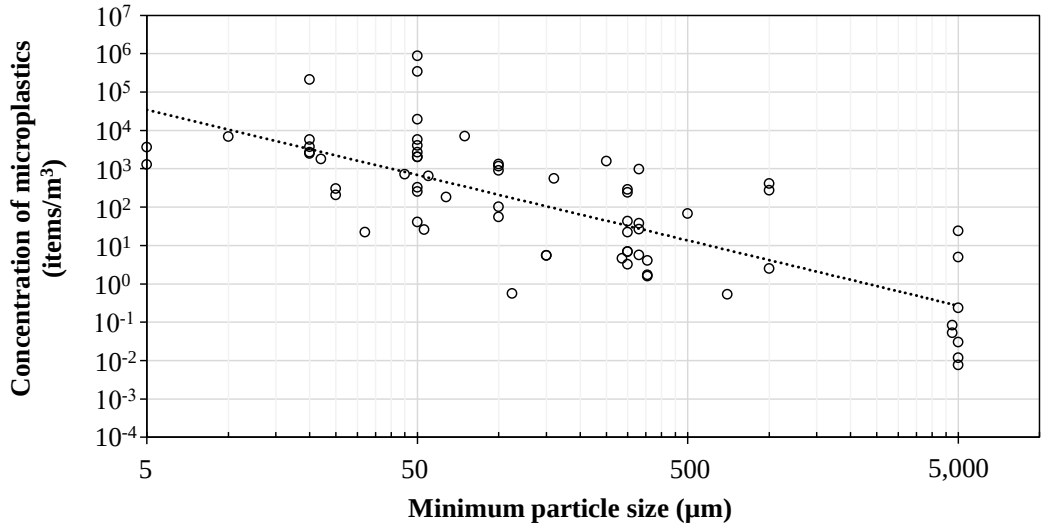


Figure 2-4 Particle size vs concentrations of microplastics in river water

(References: Alam et al., 2019; Amrutha and Warrier, 2020; Baldwin et al., 2016; Barrows et al., 2018; Campanale et al., 2020; Constant et al., 2020; Ding L et al., 2019; Dris et al., 2015; Eo et al., 2019; Fan et al., 2019; Faure et al., 2015; Gallitelli et al., 2020; Han et al., 2020; Irfan et al., 2020; Jiang et al., 2019; Kapp et al., 2018; Kataoka et al., 2019; Lahens et al., 2018; Lenaker et al., 2019; Lestari et al., 2020; Lin et al., 2018; Luo et al., 2019; Mani et al., 2015; Mani et al., 2019; McCormick et al., 2016; Miller et al., 2017; Moore et al., 2011; Mughini-Gras et al., 2021; Napper et al., 2021; Pariatamby et al., 2020; Park et al., 2020; Rodrigues et al., 2018; Rowley et al., 2020; Scherer et al., 2020; Sekudewicz et al., 2021; Singh et al., 2021; Su et al., 2018; Tien et al., 2020; Van der Wal et al., 2015; Vermaire et al., 2017; Wagner et al., 2019; Wang et al., 2017; Wang et al., 2020; Wong et al., 2020; Wu P. et al., 2020; Yan et al., 2019; Zhang et al., 2020; Zhu et al., 2019)

2.4.3 Shapes and polymer types of microplastics

The shapes and polymer characteristics of plastics may hint at the likely sources of origin of the plastics. Microplastic research has utilized various terminologies to classify the shapes in which microplastics occur in rivers (refer to Section 2.3.3). Based on a generalized classification, Figure 2-5a presents the relative abundance of the dominant microplastic shapes (fragments, fibers, spheres, films) in the surface water of rivers worldwide. As highlighted throughout this review, fibers represent the dominant shape of microplastics in river water (43%) compared to other shapes. Next to fibers, fragments indicated higher shares, which is equivalent to the total proportions of films, foam, pellets, and other shapes.

Plenty of studies attributed the higher proportions of fibers to the inputs of synthetic textiles, primarily via wastewater effluents from sewage treatment plants and atmospheric transmissions (Dris et al., 2018). Laboratory experiments have shown that fibers are easily entrained within the river flow and kept in buoyancy due to their larger

relative surface area and uneven settling (Waldschläger et al., 2020). Meanwhile, spheres, and other irregular shapes are quickly settled and accumulate in sediments. Some studies reported a dominant presence of fragments (>50%), indicating degradation of larger plastic products (secondary origin), mostly packaging material and single-use plastics (Bai et al., 2022; Lahens et al., 2018). Simultaneously, the lower presence of fibers in these studies could also be related to the deficiencies in the analytical methods to detect microplastic fibers alongside microplastic particles.

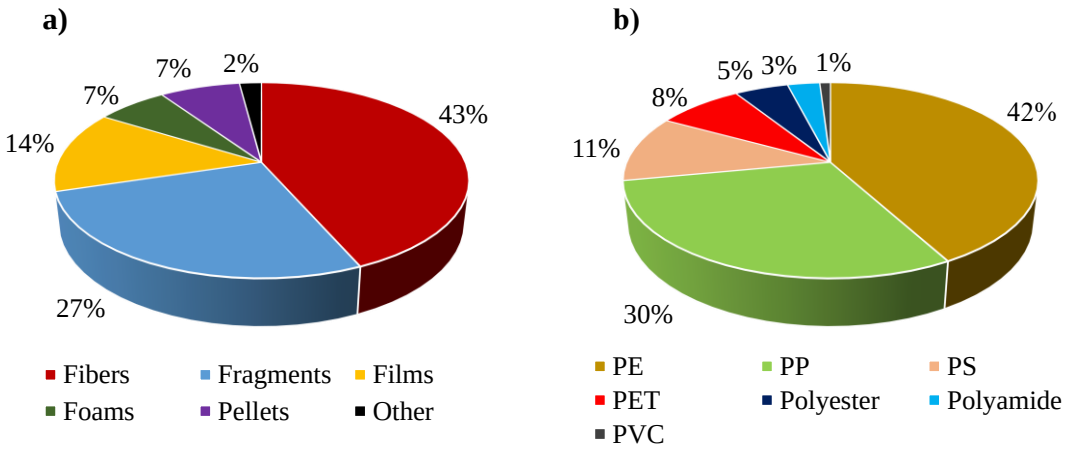


Figure 2-5 Different a) morphologies and b) polymer types of microplastics detected in river water (same references from Figure 2–4)

In terms of the polymer types, river water is found to be dominant in polyethylene (PE) (42%) > polypropylene (PP) (30%) > polystyrene (PS) (11%) (Figure 2-5b). The other frequently detected polymer types involved poly(ethylene terephthalate) (PET), polyamide, polyester, and PVC. Although not indicated in Figure 2-5b, acrylic, polyamide (PA), polyurethane (PU), and polyvinyl alcohol (PVA) have also been detected less frequently in river water. The distribution of major polymer types also reflected the global demand for plastic polymers, indicating (PE > PP > PVC > PET > PS) (Bai et al., 2022; Geyer et al., 2017). Higher occurrence of PE, PP, and PS in river water is presumed to be linked to their low densities and frequent applications in single-use plastic products including food packaging (Bai et al., 2022). Subsequently, the higher densities of polymers like PET, PVC and acrylic may explain why they are found in higher abundance in benthic sediments than in water column (Bai et al., 2022). The likely sources of other polymers involved plumbing material (PVC), synthetic textiles (acrylic

and PA), and road markings (acrylic) (Andrady, 2015; Yukioka et al., 2020). The distribution of shapes and polymer types in river water may rely on a multitude of factors explained in Section 2.4.4.

2.4.4 Factors affecting the transportation of microplastics in rivers

The mobility of microplastics entering the rivers through various sources and pathways may depend on the relative density of the particles (Waldschläger et al., 2020). Plastics of lower densities than water may float in the water surface or mobilize toward tranquil water environments, whereas denser particles may deposit in the bottom sediments (Nizzetto, Bussi, et al., 2016). Typically, the distribution and mobilization of microplastics in the water environment is found to be affected by the physical properties of the particles (size, shape, polymer type, and density), flow dynamics, biofilm formation, and aggregation of microplastics (Mani et al., 2019). Lentic water environments like reservoirs and lakes are more prone to retain microplastics through strong sedimentation compared to rivers (Boucher et al., 2019). In river systems, obstructions to flow regime by man-made hydraulic structures and natural barricades (e.g., riparian vegetation), river morphology, and geographic factors may heavily impact the distribution and transportation of microplastics (Bai et al., 2022). Moreover, hydrological conditions such as “hyporheic exchange” and “turbidity currents” may promote the partitioning of microplastics between the water and sediment phases, controlling their export downstream.

Weather factors also play a crucial role in governing microplastic mobilization in rivers. Lebreton et al. 2017 showed that over 74.5% of the total river plastic inputs to global oceans is found to occur between May and October, the wet season of the Asian and African regions, indicating the influence of weather patterns on microplastic emissions. Rainfall events in particular are recognized as the key moments of microplastic emissions in the rivers which facilitates significant microplastic inflows via runoff within a matter of few seconds (Hitchcock, 2020). Nevertheless, the impacts of rainfall on riverine microplastic emissions have been poorly clarified up to date and the existing evidence on this will be further discussed in Section 2.6.

2.5 Microplastic pollution of rivers by point source vs non-point sources

Microplastics generated from numerous anthropogenic activities enter the riverine ecosystems through a multitude of pathways, which are broadly categorized as point sources (stationary sources), and non-point sources (diffused sources) (Yano et al., 2021). Effluent outfalls of wastewater treatment plants (WWTPs) are recognized as the key point sources of microplastics in urban agglomerations (Carr, 2017; Murphy et al., 2016), in which the discharges occur through specific outlets, providing easy monitoring, controlling, and remediation of microplastic emissions (Schmidt et al., 2020). Additionally, combined sewer overflows (CSO) and storm drains also act as point sources during the occurrence of rain (Horton & Dixon, 2018). On the contrary, the emissions via non-point sources mainly involve stormwater runoff carrying microplastics deposited on the land (also referred to as urban or agricultural runoff depending on the land use) (Gasperi et al., 2014), atmospheric depositions (Dris et al., 2018), and leachate from landfills. These emissions are dispersed over a wide area, and thus, are difficult to be monitored or regulated.

The studies to date have widely investigated wastewater effluents, CSOs and stormwater runoff as crucial sources impacting the microplastic pollution of rivers. Through the stepwise treatment processes involved in WWTPs, large proportions of microplastics are removed from wastewater with almost 95–99% of removal efficiency before discharging into rivers (Mason et al., 2016; Murphy et al., 2016; Sun et al., 2023; Ziajahromi, Neale, et al., 2017). Regardless of the high removal rates, a substantial amount of microplastics is transferred to the rivers as evident from higher microplastics detected in downstream (17.93 particles/m^3) of the WWTPs than upstream (0.81 particles/m^3) (Mccormick et al., 2016). Specially, microplastic fibers are found to be poorly removed by WWTPs, and hence released to the receiving waters at higher quantities (W. Liu et al., 2021). Stormwater runoff and CSOs on the other hand exclusively occur during rainfall events (Mason et al., 2016; Sun et al., 2023), releasing exceptionally high microplastic levels into rivers and other freshwater sources, which will be further discussed in Section 2.6.

The existing evidence suggests microplastic abundances (in the size range of 20–5,000 µm) spanning between 0.28–3.14 × 10^4 particles/L in untreated wastewater, 0.01–2.97 × 10^2 particles/L in treated wastewater effluents, and 0.30–8.58 × 10^3 particles/L in surface runoff, suggesting rather high microplastic emissions through untreated

wastewater, followed by surface runoff, compared to treated wastewater effluents (W. Liu et al., 2021; C. Wang et al., 2022). Only a few studies so far have compared microplastic abundances in wastewater and stormwater within a single study area. For instance, Bailey et al. (2021) showed that microplastic abundances (in the size range of 500–2,000 µm) varied in the order, wastewater influent > storm water > wastewater effluent in Raritan Hudson Estuary, USA. Cho et al. (2023) reported significantly high microplastic concentrations (in the size range of 20–5,000 µm) in stormwater samples from an industrial (68–568 items/L) and a residential (54–639 items/L) catchment compared to WWTP effluents 0.39 ± 0.16 particles/L from Nakdong River basin, South Korea. Furthermore, several studies indicated a higher contribution to the annual microplastic loads discharge from urban catchments by stormwater runoff/CSOs than WWTP effluents: urban runoff accounted for 62% of the total microplastic emissions in Baltic Sea (Schernewski et al., 2021); and microplastic loads conveyed through CSOs was six times higher than that the same disposed through WWTP effluent in a small urban center in Shanghai city, China (Chen et al., 2020). Such findings infer that surface runoff represents the greatest conduit for MP transfer to the aquatic environment, especially in the urban areas where anthropogenic activities are intensive.

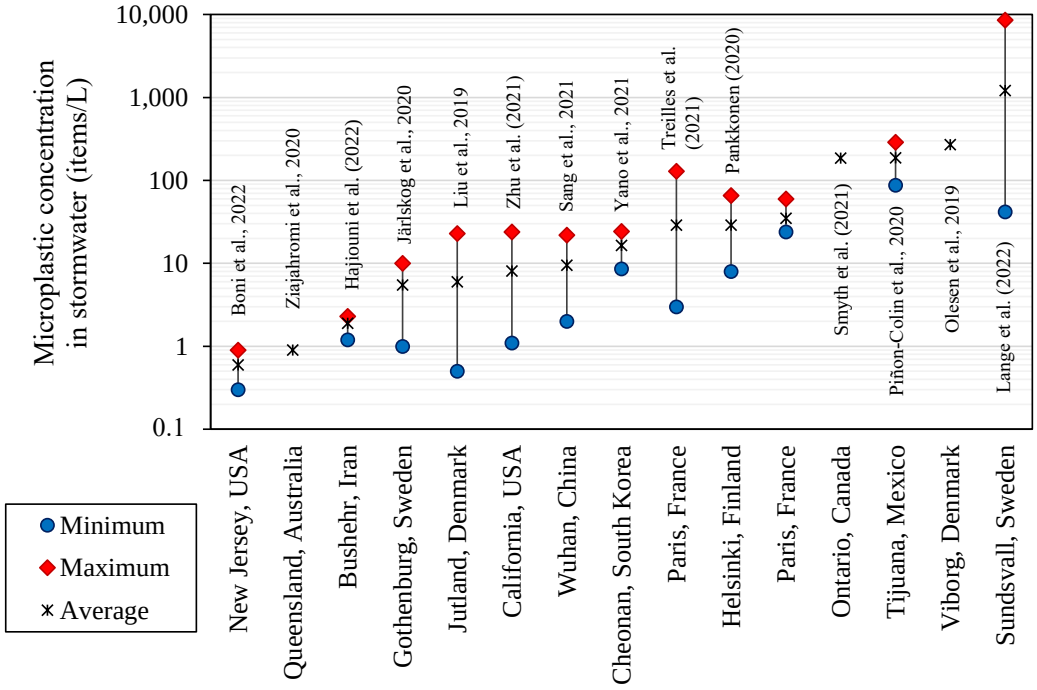


Figure 2-6 Microplastic concentrations reported in stormwater or surface runoff samples collected from various urban cities

Surface runoff facilitates the mobilization and transport of large quantities of land-sourced microplastics, along with a multitude of other pollutants (Shruti et al., 2021; C. Wang et al., 2022). Plenty of studies from the recent past revealed largely varying abundances, characteristics, and distribution of microplastics in surface runoff. Figure 2-6 depicts microplastic concentrations reported in urban runoff from various countries/cities worldwide. The concentrations ranged between 0.3 items/L (minimum) to 8,580.0 items/L (maximum), where the lowest and the highest concentrations were reported from the USA and Sweden, respectively. It is quite difficult to compare the microplastic levels in runoff sampled from different countries, owing to the disparities in land use and rainfall patterns, as well as the methods used in microplastic sampling and analysis (C. Wang et al., 2022). Additionally, the highest concentrations reported so far were noted for very small particle sizes, indicating the necessity to include small particle sizes in the analyses of microplastics in surface runoff. The existing data are largely from developed countries whilst there is limited data available from developing countries (Figure 2-6). However, microplastic abundances (in the size range 0.1–5 mm) in road dust sampled from Vietnam (19.7 pieces/m^2), Nepal (12.5 pieces/m^2) and Japan (2.0 pieces/m^2) has portrayed significantly higher contents in the samples from developing countries than developed countries (Yukioka et al., 2020). Road dust represents a vast reservoir of microplastics in urban cities which are likely mobilized through surface runoff during the onset of rainfall events. The higher microplastic levels in the road dust from under-developed areas owing to a higher degree of plastic waste mismanagement may lead to potentially high microplastic levels in urban runoff as well.

2.6 Microplastics in runoff and its implication on riverine environments

Rainfall and subsequent surface runoff events are considered the primary mobilizing processes for numerous non-point source pollutants including nutrients, and pathogens. Therefore, the early research on microplastics also hypothesized the involvement of similar dynamics in the transport of microplastics in terrestrial and aquatic environments (Hitchcock, 2020). Storm events in particular, have shown to impact microplastic loading in both marine and freshwater systems significantly (Gündoğdu et al., 2018; Moore et al., 2011). Relatively more of these studies were focused on still water environments like lakes and bays, where increased microplastic fluxes were observed with rainfall (W. Xia et al., 2020). Nevertheless, rather dynamic microplastic abundances

have been noted in moving waters like rivers, during as well as following rainfall events. Additionally, these events have shown to reorganize the distribution of microplastics in river water environments (Wei et al., 2022). A list of past studies that investigated the effects of rainfall events on microplastic abundances in rivers are shown in Table 2-2. These studies involved sampling of microplastics in river water before, during and after rainfall events, and among different seasons, at varying sampling frequencies.

2.6.1 Effects of rainfall events

Cheung et al. (2019) sampled microplastics in surface water Lam Tsuen River, Hong-Kong, after a three-day rainfall event, and found that the abundances were dropped by an order of magnitude (from 14.0 to 1.3 pieces/m^3) within two hours. Microplastic abundance in Cooks River estuary, Australia was raised by 40-folds during a storm event, compared to before (Hitchcock, 2020). Interestingly, flooding mobilized approximately 70% of the microplastic mass deposited within the riverbeds flowing a flooding event in Mersey and Irwell catchments in Northwest England, giving rise to increased microplastic levels in the water phase (Hurley et al., 2018). Moreover, a flood event that represented 14.5% of the year (in terms of days per year) contributed to ~40% of the annual mass fluxes of both microplastic particles and fibers in the Seine River basin, France (Treilles et al., 2022). These results manifest the highly dynamic temporal distribution of river microplastics during /following rainfall events. Additonally, inter-event microplastic data have indicated positive correlations between precipitation and the numerical concentrations of microplastic in rivers, indicating rainfall and storm events as the key moments of microplastic contamination (Hitchcock, 2020).

Regarding the impacts on the distribution of microplastics in riverine environments, MPs derived from road marking paints in urban runoff have been detected in sediments of tributaries of the River Thames, UK, at an order of magnitude higher abundance than the water column (Horton et al., 2017). Wei et al. (2022) reported noticeable differences in the size distribution and polymer composition of the microplastics stocks in the Qing River, China by sampling before and after a rainfall event. Similarly, Sugiura et al. (2021) illustrated the contribution of street runoff to the microplastic inputs in estuarine water of Sumida River, Japan by highlighting significant inflows of polyethylene polypropylene diene (PEPD) through runoff.

Table 2-2 Effects of rainfall-runoff events and seasonal variations on microplastic contamination of rivers

Location	Size (mm)	Type of sample [a]	Units	Microplastic concentration		sampling frequency	Reference
				Minimum	Maximum		
Lam Tsuen River, Hong-Kong	0.35–4.75	rain	items/m^3	1.3	14.0	On the third day of a continuous rain-fall event	Cheung et al., 2019
Nakdong River, South Korea	0.02–5.00	dry and wet	items/m^3	293	4,760	Monthly sampling for four months	Eo et al., 2019
Cooks River estuary, New South Wales, Australia	0.05–5.00	rain	items/m^3	400	17,383	Three times prior to the storm, daily for the first two weeks after the storm, then every four days for the subsequent three weeks.	Hitchcock et al., 2020
10 rivers in Northwest England	0.30–5.00	rain	items/m^2	1,428	517,142	Once before and once after a flood	Hurley et al., 2018
Xindian River, Northern Taiwan	0.30–5.00	-	items/m^3	2.5	83.7	Once every two weeks for three-months' time (including one heavy rainfall event)	Wong et al., 2020
Seine River, France	1.00–5.00	wet (MPF)	items/L	1.3	3.7	During a strong flood event, which represented 14.5% of the year (in terms of time); sampled twice during flooding in upstream and downstream; and during dry period	Treilles et al., 2022
		wet (MP)		10.4	34.4		
		dry (MPF)		1.9	5.5		
		dry (MP)		9.3	26.5		
Maozhou River, China	0.01–5.00	dry	items/L	4.0	25.5	Dry and wet season sampling (not sampled during rain)	Wu et al., 2020
		wet		3.5	10.5		
Manas River Basin, China	0.10–5.00	dry	items/L	14	22	Dry and wet season sampling (not sampled during rain)	G. Wang et al., 2021
		wet		10	19		
Sumidagawa River Estuary, Tokyo, Japan	0.01–5.00	dry	items/L	1.4	2.3	During a continuous rainfall event that lasted for 48 h (preceding rainfall of 86 mm)	Sugiura et al., 2021
		wet		1.8	4.3		
Yellow River, China	0.05–5.00	dry and wet	items/L	380	1,392	Two times (each) in dry and wet seasons	Han et al., 2020

[a] "*dry" and "wet" refer to samples collected during dry and rainy seasons, respectively; "rain" refers to samples collected during the occurrence of rain; "MP" and "MPF" refer to microplastic particles and fibers, respectively.*

Since the abundances and characteristics of microplastics indicate significant temporal changes related to precipitation patterns, sampling time and frequency is critical in capturing the highly dynamic microplastic flows in the river systems (Cheung et al., 2019; Hitchcock, 2020). Additionally, from the learnings of runoff studies, it is obvious that microplastic fluxes are highly dependent upon various rainfall characteristics involving rainfall intensity, antecedent dry days, rainfall duration etc. However, very few studies to date have explored these aspects with sufficient sampling; therefore, further studies are needed to capture those variations at a higher time resolution involving sampling before, during, and after a rainfall event.

2.6.2 Seasonal variations

Understanding the seasonal variations in plastic transport in the riverine ecosystem is found to be beneficial in monitoring and planning mitigation strategies for plastic pollution (Van Emmerik et al., 2019). In a model-based study, Lebreton et al. (2017) assessed seasonal variations in river plastic inputs into the global oceans using monthly averaged daily runoff data for nine consecutive years and showed that over 74% of the total river plastic inputs occur between May and October, indicating links with rainfall patterns, particularly of Asian and African regions. Seasonal variations of microplastic abundances indicated contrasting results between dry and rainy seasons.

A great number of studies reported increased microplastic concentrations during the wet season than the dry season as anticipated from microplastic inflows through runoff emissions. For instance, the microplastic abundance in Los Angeles River, USA was 5 items/m^3 in the dry season compared to 153 items/m^3 in the rainy season (Moore et al., 2011); in Venoge River, Switzerland, 150-times increment in microplastics contents was observed in the wet period (Faure et al., 2015); similarly, the microplastics abundance increased from 0.9 in dry seasons to 13.0 items/m^3 in wet season in the Ofanto River, Italy (Campanale et al., 2020), and lastly, Qiantang River, China also depicted increased abundance from dry to rainy season (889 to 1,607 items/m^3 increment) (Zhao et al., 2020).

In contrast, some studies reported that the dry season has more microplastic contents than the rainy season (Table 2-2). For example, the average abundances of microplastics in the dry and wet seasons were 930 and 497 items/L, respectively in the Lower Yellow River near the estuary, China (Han et al., 2020). Additionally, the

abundance of microplastics in Maozhou River, China in the dry season (4.0–25.5 items/L) were relatively higher than the levels observed in the wet season (3.5–10.5 items/L) (Wu et al., 2020). Manas River, China also depicted higher microplastic abundance in the dry season than in the wet season (G. Wang et al., 2021). Although, understandably, microplastic abundances are higher in dry periods than wet periods, microplastic loads/fluxes should be considered to evaluate the real impact of seasonality on microplastic pollution. This is evident from the data showcasing higher contribution to annual microplastic loads in the Nakdong River, South Korea by the emissions in the wet season (70–80%) than in the dry season (Eo et al., 2019).

2.7 Summary and the gaps in existing research

Microplastics are pervasive in riverine environments worldwide and mobilize over long distances along the river flows, ultimately leading to the marine pollution of microplastics. The intrinsic properties of these small particles together with the complex fluvial processes in the river systems significantly influence their mobility, resulting in heterogeneous spatiotemporal distribution patterns for microplastics. Therefore, the existing studies have shown a high diversity in the abundance, shape, size, and polymer types of microplastics in such environments. The abundances of microplastics detected in the surface waters of rivers worldwide vary up to eight orders of magnitude (20–5,000 µm), depending on the geographic locations and the land use patterns. The research to date has mostly investigated microplastic pollution characteristics in the river systems in China, Europe, and North America. Nevertheless, it is imperative to explore the situation in other parts of Asia, and also in South America, particularly considering the high plastic waste mismanagement in the low-income economies of those regions.

In terms of the size of plastic debris, the existing studies have predominantly focused on microplastic particles that are particularly larger than 300 µm, compared to larger plastic debris (mesoplastics or macroplastics) as well as the microplastics smaller than 300 µm. Considering the continuous fragmentation of plastic debris due to various environmental processes and also the implications of tiny microplastics (including nanoplastics) on the aquatic biota, it is vital to understand the distribution of these particles on an extended continuum of particle size. Although higher abundances of microplastics have been reported at lower particles sizes of microplastics, the limited capacity of the existing analytical methods to detect the numerical quantities of small

microplastics (usually <10 µm) is a concern. Additionally, the lack of knowledge on the mass-based abundances of microplastics is a challenge for quantifying the magnitude of microplastic emission at the catchment/regional scale. The discrepancies in the methods involved in microplastic sampling, extraction, and analysis; and the units of reporting the abundances of microplastics make it challenging to derive meaningful comparisons between the existing microplastic studies. Therefore, it is crucial to establish standardized and reproducible procedures, involving appropriate quality assurance and quality control protocols to facilitate reliable comparisons between the studies.

Despite the aforementioned knowledge on riverine microplastics, their transmission into the receiving waters through numerous sources and pathways is still poorly understood. For instance, the contribution of non-point sources such as surface runoff and atmospheric fallouts to the microplastic emissions in rivers has been rarely explored compared to point sources like treated wastewater effluents. Storm events are recognized as key moments of microplastic pollution in freshwater environments, yet there is little understanding of the real-time dynamics of microplastic emissions in rivers during such events. Moreover, the current knowledge is limited to the relative contribution of various sources and pathways to the annual microplastic releases from riverine catchments. Such information is imperative for determining control strategies for microplastic pollution of not just riverine ecosystems, but also global oceans. A thorough understanding of the dynamics, distribution, behavioral patterns, and fate of microplastics in riverine ecosystems is yet to be unveiled through field observations and modeling studies on regional as well as global scales. This in turn would help formulate policies, regulations, and strategies for systematic abatement of microplastic pollution of aquatic environments globally.

CHAPTER 3. Occurrence and distribution of plastic particles (10–25,000 µm) and microplastic fibers in the surface water of an urban river network in Japan

3.1 Introduction

The rapid population growth, technological advancements, and improving economies demand a rise in the production and consumption of plastics worldwide. Global plastics production reached 390.7 million tons at the end of 2021, and nearly 80% of these plastics are likely to end up in landfills or the natural environment owing to poor waste management practices (Geyer et al., 2017; Plastic Europe, 2022). Oceans are considered the ultimate sinks of land-sourced plastic wastes, with small urban rivers acting as the major conduit of those plastics to the oceans (Lebreton et al., 2017; Meijer et al., 2021), via various means (Dris et al., 2016; Hitchcock, 2020; Jambeck et al., 2015; Lusher et al., 2015; Murphy et al., 2016). Once introduced into the river environments, plastics may deposit on the flood plains and riverbanks, sink into the riverbed, or pass onto the receiving waters through the river flow (Kataoka et al., 2019). Subsequently, plastics undergo gradual degradation and successive fragmentation due to UV radiation, oxidation, mechanical abrasion, and biological effects (Andrady, 2015; Ter Halle et al., 2016; Zbyszewski et al., 2014). These fragments are generally categorized by their sizes, into macroplastics (>25 mm), mesoplastics (5–25 mm), microplastics (<5 mm), and nanoplastics (<1 µm) (Andrady, 2015; Horton et al., 2017).

Microplastics (MPs) have been regarded as an emerging pollutant, threatening aquatic lives and human health (Eerkes-Medrano et al., 2015; L. Lu et al., 2019; Wilcox et al., 2015). Occurring in various shapes in the environment, MPs can originate from either primary factory-made plastics found in personal care products, fertilizers, paints, detergents, and cleaning products, or the secondary fragmentation of larger plastics (Andrady, 2015; Cole et al., 2011; Jambeck et al., 2015), and largely exist in the form of microplastic fibers (MPFs) (Dris et al., 2016, 2018) due to the abundant release in laundering processes (Carr, 2017; Napper & Thompson, 2016; Vassilenko et al., 2021; Zambrano et al., 2019), and break-through from wastewater treatment plants (WWTPs) into effluents entering the riverine systems (Ben-David et al., 2021). Some environmental concerns of MPs and MPFs include the transfer of adsorbed toxic elements, such as

persistent organic pollutants (POPs) and heavy metals into biota (Bakir et al., 2016; Cole et al., 2011; McLaren et al., 2004); gut system obstructions, oxidative stresses, and cell damages through ingestion chains (Iannilli et al., 2019; L. Lu et al., 2019; Mizraji et al., 2017; Rebelein et al., 2021; Wilcox et al., 2015; Ziajahromi, Kumar, et al., 2017).

Considering the increasing risk of MPs on aquatic lives and the vital role that rivers play in conveying land-originated plastics in the oceans, numerous studies have explored the occurrence and distribution of MPs in riverine environments worldwide (Blettler et al., 2018; Kumar et al., 2021). However, a majority of these studies assessed MPs larger than 300 µm in size, a non-standard threshold established by the mesh size of the plankton nets that are commonly used in MP sampling (Faure et al., 2015; Mani et al., 2015; L. Zhang, Liu, et al., 2020). Research on much smaller particles is rare as it demands advanced analytical methodologies and instrumentation (E. Miller et al., 2021). On the other hand, the attempts to analyze mesoplastics are also limited due to the difficulties of sampling large volumes of water. Exploring the spatial and temporal distribution of fluvial plastic particles over a broad and continuous size scale that extends beyond micron size (from macro- to nano-plastics) is vital for providing a better understanding of plastic pollution, given that smaller particles are largely derived from the fragmentation of larger plastics (Horton et al., 2017). Furthermore, MPFs have received little attention in MP research, despite their ubiquity and abundance in the environment, due to the discrepancies in analytical methods and cross-contamination challenges associated with sampling and analysis (Rebelein et al., 2021).

The present study intends to cover the above-mentioned gaps in existing research by investigating plastic pollution in an urban river network in Japan over a broader spectrum of size and shape. As a developed country that single-handedly contributes to around 4% of global plastic production, Japan possesses only a few published research on MP pollution of its aquatic environments (Plastic Europe, 2022). While Isobe et al. (2015) and Kabir et al. (2020) focused on the coastal beaches of the Sea of Japan (SJ) and the Seto Inland Sea (SIS), only a few published research to date investigated riverine MPs in Japan (Kabir et al., 2021; Kameda et al., 2021; Kataoka et al., 2019). These studies, however, provided little information on mesoplastics, MPs smaller than 50 µm, or MPFs.

The present study explored the primary river network across Kyoto City, one of Japan's largest and most densely populated cities, depicting a perfect fit for an urbanized watershed. The specific objectives of the study were;

1. to investigate the magnitude and characteristics of plastic pollution and their spatial distribution in an urban river network in Japan, based on a wide size range of plastic particles and fibers;
2. to compare the pollution levels in Japanese rivers with those reported from other parts of the world; and
3. to estimate the total plastic loads being conveyed through the river network during a typical dry day.

This study marks the first attempts to assess plastic debris of a wide size range, spanning between 10 µm MPs to 25 mm mesoplastics, and MPFs in a single study related to inland rivers worldwide. It will add to clarifying the contribution of Japan to the global pollution of plastics in freshwater, and its consequences on the North Pacific Ocean and adjoining maritime zones; and will provide useful archives for developing control strategies against MP pollution in the future. Appendix A provides the supplementary information relevant to this study which shall be referred to in conjunction with Chapter 3.

3.2 Materials and methods

3.2.1 Study area

The study area included the river network of Kyoto City in Japan, comprising its two major rivers, Katsura and Kamo (Figure 3-1). It covers 30% of the entire catchment of Katsura River (107 km long; 1160 km^2 catchment area), in which Kamo River (31 km long; 210 km^2 catchment area) is a sub-basin. The riverbanks of Kamo River are popular among tourists and locals for viewing cherry blossoms (Sakura), fishing, and strolling. On the other hand, the flood plain of Katsura River accommodates acres of agricultural land and is famous for holding barbecues during summer. Originating in the northern region of Kyoto, the two rivers flow towards the south to combine at Shimomukōjima-cho. Afterward, the Katsura River becomes a major tributary to the Yodo River, which falls into the sea at Osaka Bay. Yodo River is the primary source of drinking water for over 11 million population in downstream (Lein et al., 2008). The study area is located within the heavily built-up zones of Kyoto City, as shown in Figure 3-1a. It is home to nearly 1.5 million inhabitants, with a population density of 1,782 persons/km^2 (Kyoto City, 2020). These urban areas are connected by public sewer systems with 99.5%

coverage (JSWA, 2021). Additionally, all industrial wastewater generated within the watershed is discharged via WWTPs. The two WWTPs of the city are discharging treated effluents to both the Kamo and Katsura Rivers towards the downstream of the river network Figure 3-1(b).

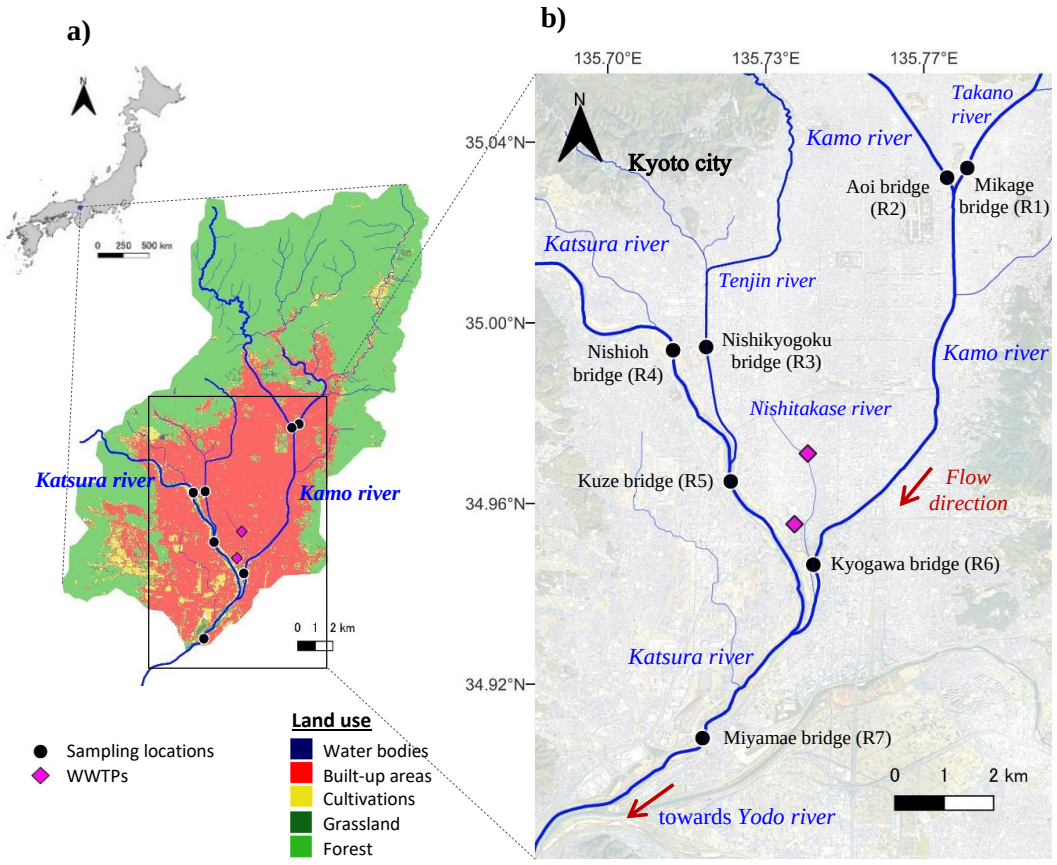


Figure 3-1 a) Land use map of the study area; b) River network of the study area and sampling locations (R1 – R7) in Kyoto City

3.2.2 Sample collection

Two sampling campaigns were conducted in August and October 2021, under the dry weather conditions of late summer (temperature: 25–32 °C). The first survey was conducted after three antecedent dry days whereas the second after eleven antecedent dry days. Samples were collected at seven sites (Figure 3-1 and Table A–1), including three stations along the Kamo River (Mikage bridge-R1; Aoi bridge - R2 and Kyogawa bridge - R6) and four along the Katsura River (Nishikyogoku bridge - R3; Nishioh bridge - R4; Kuze bridge - R5 and Miyamae bridge - R7). For the convenience of data analysis, the entire river network was divided into three sections: Upstream (R1, R2, R3, and R4),

Midstream (R5 and R6), and Downstream (R7). Plastic samples were collected using plankton nets of different mesh sizes, depending on the target particle size of plastics as follows.

Mesoplastics (5,000–25,000 μm) and large MPs (300–5,000 μm): Sampling for mesoplastics (hereinafter referred to as "MesoPs") and large MPs (hereinafter referred to as "LMPs") were achieved with plankton nets of 1 mm and 300 μm mesh sizes, respectively (0.3 m Ø opening and 1 m length), deployed from bridges. The plankton nets were laid parallel to the flow, at the surface of the river, for approximately 6 hours for the collection of MesoPs, and 30 minutes for LMPs. The submerged depth of the nets was noted, and the flow rate at which water passed through each net was monitored using a propeller-type current meter. At the end of sampling, the nets were retrieved, and the debris trapped inside the nets were carefully washed into pre-rinsed 1 L glass bottles and stored in a cooler box until transportation to the lab.

Small MPs between 10–300 μm (hereinafter referred to as "SMPs"): The samples were collected by in-situ pump filtration method using a 12V DC submersible pump. The pump was submerged at ~30 cm below the river's water surface and operated from the bridge at a constant speed. The pump's inlet and outlet were covered with 300 μm and 10 μm mesh-sized Nylon plankton nets, respectively, to allow the filtration of 10–300 μm particles only. The flow rate (in L/s) was recorded during sampling. Subsequently, the 10 μm net was carefully removed and stored in a re-sealable bag until transportation to the lab.

Microplastic fibers of 10–5,000 μm length (hereinafter referred to as "MPFs"): Sampling was done by manual filtration of 20 L of water fetched from the top 30 cm of the river surface, using a stainless-steel bucket. The water was then filtered through a plankton net of 10 μm mesh size, which was carefully transferred into re-sealable bags at the end of sampling.

3.2.3 Extraction of plastics

Plastic particles (MesoPs, LMPs, and SMPs) were extracted using a method similar to Mintenig et al. (2020) and Rodrigues et al. (2018) with certain modifications. Firstly, the organic matter in the samples were removed via wet peroxidation method using 30% H_2O_2 (Wako Pure Chemical Corporation, Japan) and 0.05 M $FeSO_4$, followed

by oven drying at 55 ℃ for a few days (Mintenig et al., 2020; Rodrigues et al., 2018). Then, density separation was performed using 5.3 M NaI (1.53 g/cm^3) to remove the sediments contained in the samples, resulting from the shallow depths of the rivers. MesoPs and LMPs were recovered from the surface of the NaI solution through vacuum filtration using a 10 µm nylon net. For extraction of SMPs, the density separation process was repeated twice under centrifugation, and the supernatant was vacuum-filtered through a 0.45 µm membrane filter. The filtrate was carefully transferred to and stored in a 100 mL glass bottle containing Ethanol (95.1–96.9 vol%; Kaneichi Pharmaceuticals, Japan).

MPFs were isolated by fluorescence staining with Nile Red (NR) dye, a method extensively used to detect MP particles in various environmental matrices (Shruti et al., 2022). However, its applications on MPFs are limited. The present study employed a method similar to Shim et al. (2016). The samples were digested with 30% H_2O_2 following the same procedure employed on SMPs. However, density separation was not conducted. The digested samples were vacuum filtered through a 10 µm polycarbonate (PC) membrane (47 mm ∅). After that, 5 mL of 2 M HCl was applied over the filter for further removal of the remaining organic matter and lipid contents, and thereby improving the visibility of NR staining. HCl was left to absorb to the filter for 5 mins and removed via vacuum filtration. Subsequently, 200 µL of 1 mg/mL NR solution (NR powder and acetone mixed at a 1:1 ratio) was added to the filter and left to absorb for 15 mins. Next, NR was also filtered out, and the PC filter was placed upside down in 20 mL of ultrapure water (Milli-Q® Reference A+ System, Millipore Corporation, USA) in a glass beaker and subjected to ultrasonication for 5 mins to transfer all the stained residues into water. This procedure was meant to avoid excess dye binding and thereby improve the efficiency of MPF detection while avoiding overestimation (Shruti et al., 2022). The solution in the beaker was filtered through a new 10 µm PC membrane, which was left to air-dry and covered with a clean glass slide for microscopic examination.

3.2.4 Characterization of plastics

MesoPs and LMPs were examined using a stereoscopic microscope coupled with a digital camera (SMZ-161 Series, Shimadzu, Japan) to determine the particle size, shape, and color. Depending on the morphological features, MPs were classified as fragments, fibers, films, and spheres, and when a particle could not be classified under any of these

shapes, it was considered a “fragment” (Yan et al., 2019). The polymers were identified by Agilent Cary 600 Series Fourier Transform Infrared Spectrometer (Cary 630 FTIR, Agilent Technologies, USA) equipped with attenuated total reflectance (ATR) based on the recorded spectra (650–4,000 cm^{-1}) matched with an in-house spectral library. Each spectrum averaged 256 scans at a resolution of 8 cm^{-1}, and only the resulting spectra with a matching degree greater than 60% were considered valid after careful comparison with the reference spectrum of known plastics (Table A–2).

The SMPs were identified and quantified using Agilent Cary 600 Series µ-FTIR (Cary 620 microscope connected to Cary 660 spectrometer). A known volume of each SMP sample stored in ethanol was filtered through a 0.1 µm inorganic membrane filter (Anodisc, 13 mm ∅, Whatman™, USA) and left to dry overnight. Chemical mapping of the potential plastic particles was performed with µ-FTIR in transmission mode. Analysis was performed in the wavenumber range of 4,000–900 cm^{-1}, using 16 scans performed at a resolution of 4 cm^{-1}. The obtained spectra were compared with the reference spectrum databases, and the polymer types were determined by matching degrees >85% (Table A–3).

The MPF samples in glass slides were observed with an epifluorescence microscope (Stereozoom S9D, Leica Microsystems, Switzerland) under blue light conveyed through an orange-color high-pass filter (excitation wavelength: 485 nm, emission wavelength: >530 nm). The entire surface area of the PC membrane was photographed, and then the fibers that appeared in fluorescence were manually traced with Inkscape 1.0.1 software to determine the dimensions. Based on the observed colors of fluorescent fibers, MPFs were divided into three categories as “Red”, “Yellow” and “Green”. Standard observations of NR-tagged MPFs of known polymer types revealed that polyethylene terephthalate (PET) and nylon fibers may appear in “Red”; PE and PP may appear in “Green”; whereas acrylic fibers may appear in “Yellow” (Table A–4). It should be noted that these colors may represent a wide variety of polymers with similar chemistry. Additionally, non-plastic fibers such as cotton and wool were also tested upon NR-staining to confirm the validity of the results (Table A4).

3.2.5 Quantitation of plastics

The concentrations of confirmed plastics were expressed as the number of

particles per unit volume or mass per unit volume of water. The mass of the particles was calculated by multiplying the polymer density by the volume of each particle. Depending on the morphology of the particles, the volume was calculated (with Equations 3-1 and 3-2) using the following criteria introduced by Cózar et al. (2014).

$$\text{Volume of fibers} = \pi r^2 h \quad (3\text{-}1)$$

$$\text{Volume of non-fibers (fragment, films, and spheres)} = 4/3\pi r^3 \alpha \quad (3\text{-}2)$$

Where "r" is the measured radius of each fiber, and half of the average of maximum and minimum lengths of non-fibers; "h" is the measured length of each fiber; and "α" is the shape factor (0.1 for fragments and films, and 1 for spheres).

This method of calculating mass is validated in Text A–1 (along with Table A–5). In summary, the calculated masses for MesoPs would be approximately 8 times (7.5 ± 5.5 times) higher than the measured/actual masses. For MP particles in the size range of 1–5 mm, the calculated masses would be almost half the measured masses (0.5 ± 0.4 times). Additionally, the calculated mass of LMPs (300 µm – 5 mm) would be approximately 4 times (4.3 ± 4.5 times) higher than the measured masses. The method validation was not performed for SMPs as it is impossible to measure the actual mass of such small particles.

3.2.6 Quality assurance and statistical analysis

Numerous efforts were made to minimize the contamination of plastic samples from the point of sampling to chemical analysis. All plankton nets used for sampling of MesoPs and LMPs were thoroughly cleaned before use, and only new plankton nets were used for sampling of SMPs and MPFs because of the fine mesh size (10 µm). All solutions used in the experiments, such as NaI, HCl, and $FeSO_4$ were pre-filtered with 0.45 µm GF/F filters (Advantech, 47 mm ∅), and the equipment were thoroughly rinsed with ultrapure water prior to use in the experiments. The samples and labware that were used in the experiments were properly covered with aluminum foil while not in use. Additionally, all laboratory work, including sample pretreatment and processing, was always performed under a fume hood. Natural latex gloves and cotton lab wear were worn by all individuals during all laboratory procedures while completely avoiding plasticware unless absolutely necessary. In order to minimize human errors and maintain the consistency of the results, the sample analyses were always performed by the same

individuals. Lastly, combined field and procedural blanks were conducted alongside each category of plastics from field sampling to chemical analyses, and the results of environmental samples were adjusted for background contamination accordingly. The results of blank tests are shown in Table A–6 whereas the results of recovery tests are shown in Table A–7.

The data were curated and processed using Microsoft Excel, while the statistical analysis was conducted using R 4.2.1. For normally distributed data, the Welch two-sample *t*-test, One-way Analysis of Variance (ANOVA), and subsequent Tukey Honest Significant Differences (Tukey's HSD) tests were employed, whereas Mann-Whitney U test and Kruskal-Wallis rank sum test together with Bonferroni post hoc test were performed otherwise. All tests were performed at a statistical significance of $p<0.05$. QGIS ver. 3.22.11 was used for creating maps.

This study intends to compare the plastic pollution levels in Japanese rivers with those reported from other parts of the world (refer to Section 3.4.1). However, the absence of standard protocols for sampling, extraction, and the analysis of plastics could lead to inconsistent results among different studies (Horton et al., 2017); therefore, only the previous studies that employed similar analytical procedures, quantitative units, and a well-defined range of particle sizes were considered for this comparison.

3.3 Results

3.3.1 Plastic concentrations

The number concentrations and mass concentrations of the riverine plastics in August and October are shown in Table 3-1. MesoPs were not detected at R3 in August and at R2 and R5 in October. Nevertheless, all stations reported LMPs, SMPs, and MPFs. No statistically significant difference was found between the concentrations reported in August and October, as the two surveys were conducted during the same season with no preceding heavy rainfall events or extreme meteorological conditions. Therefore, the data from the two surveys were combined to estimate the concentrations at each location (Figure 3-2). In general, the concentrations of plastic particles (MesoPs, LMPs, and SMPs) gradually increased from upstream to downstream, with R7 indicating the highest concentrations most of the time, while multiple upstream stations except R1 possessed the lowest concentrations (Figure 3-2). Out of the two upstream stations in the Kamo

River (R1 and R2), R1 showed higher plastic concentrations, On the other hand, the two upstream stations of Katsura River (R3 and R4) showed comparable concentrations. The midstream (R5 and R6) showed relatively lower concentrations of larger plastics compared to the upstream of the river. Unlike plastic particles, the concentrations of MPFs slightly increased along the river and varied only within a narrow range (1,470–3,600 items/m^3 and 520–1,060 μg/m^3) (Figure 3-2). The highest MPF concentrations were also reported from the downstream (R6 for number and R7 for mass).

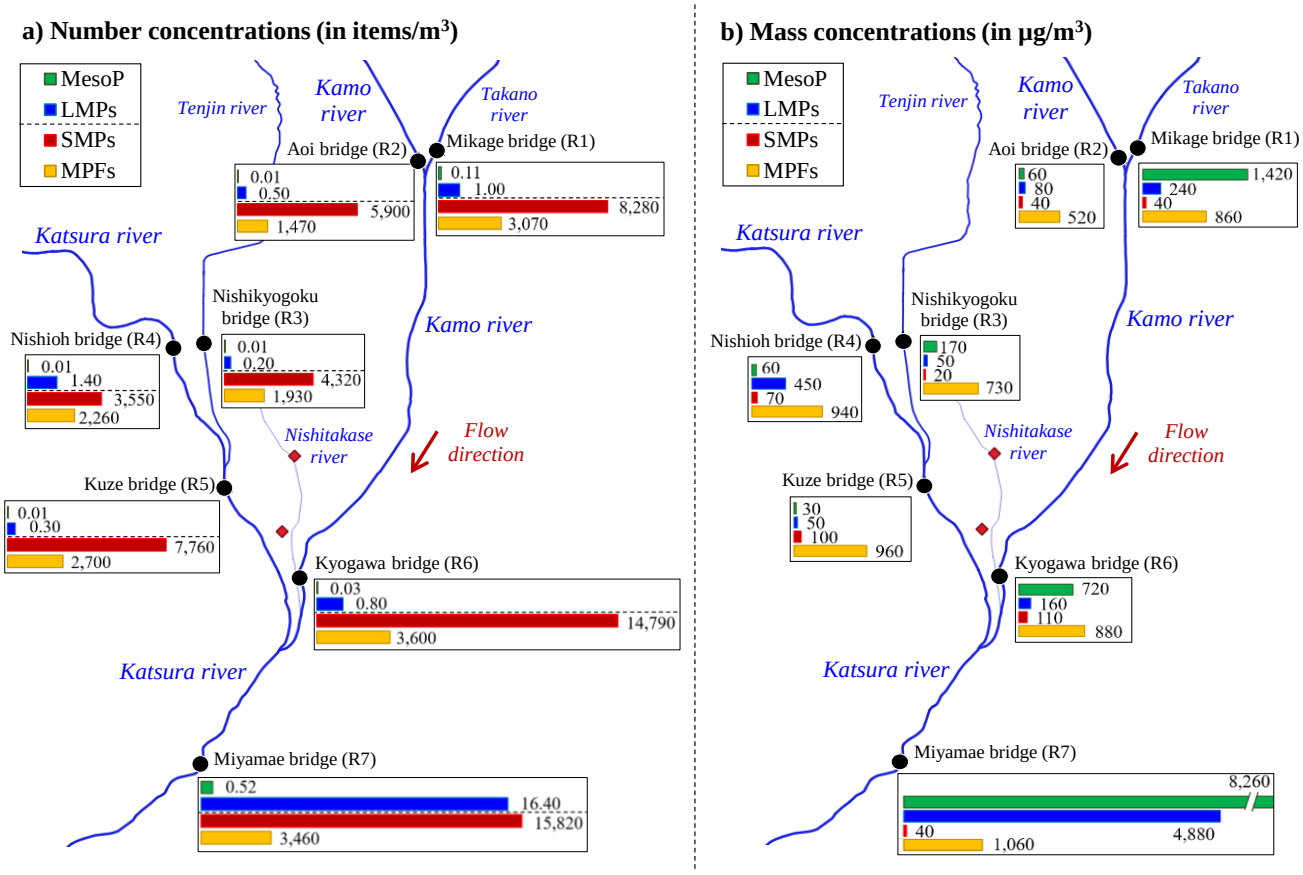


Figure 3-2 Concentrations of plastics in river water
a) Number concentrations expressed in items/m^3 (bar lengths not to scale); b) Mass concentrations expressed in μg/m^3 ("MesoPs" refers to mesoplastics in the size range of 5,000–25,000 μm; "LMPs" refers to large microplastics in the size range of 300–5,000 μm; "SMPs" refers to small microplastics in the size range of 10–300 μm; "MPFs" refers to microplastic fibers in the size range of 10–5,000 μm).

Table 3-1 Plastic concentrations reported in the two surveys

			Mikage Bridge (R1)	Aoi bridge (R2)	Nishikyogoku bridge (R3)	Nishioh bridge (R4)	Kuze bridge (R5)	Kyogawa bridge (R6)	Miyamae bridge (R7)
Survey in August	**Number concentrations (Items/m^3)**	SMPs[a]	9,370	5,320	4,020	1,570	4,980	8,720	7,070
		LMPs[b]	1.25	0.59	0.44	1.92	0.61	0.25	19.77
		MesoPs[c]	0.09	0.02	0.00	0.01	0.02	0.04	0.65
		MPFs[d]	3,110	1,670	1,640	1,420	1,700	4,250	3,930
	Mass concentrations (µg/m^3)	SMPs[a]	50	20	20	10	70	140	30
		LMPs[b]	150	100	30	530	100	5	6,420
		MesoPs[c]	2,230	90	0.00	40	50	1,040	9,660
		MPFs[d]	850	510	490	550	620	630	780
Survey in October	**Number concentrations (Items/m^3)**	SMPs[a]	7,580	6,240	4,410	4,100	8,750	20,870	25,560
		LMPs[b]	0.82	0.22	0.13	0.91	0.09	2.32	10.51
		MesoPs[c]	0.13	0.00	0.02	0.02	0.00	0.03	0.35
		MPFs[d]	3,040	1,270	2,220	3,100	3,700	2,950	3,000
	Mass concentrations (µg/m^3)	SMPs[a]	30	50	20	80	80	100	60
		LMPs[b]	320	20	50	370	10	640	2,200
		MesoPs[c]	620	0	280	80	0	500	6,350
		MPFs[d]	880	530	960	1,330	1,300	1,120	1,340

[a] Small microplastics (10–300 µm); [b] Large microplastics (300–5,000 µm); [c] Mesoplastics (5,000–25,000 µm); [d] Microplastic fibers (10–5,000 µm)

3.3.2 Particle size distribution of plastics

The particle size distribution of plastic particles and MPFs with respect to their number and mass were derived based on the analysis of 2,657 plastic particles and 911 fibers. It is evident from Figure 3-3a and Figure 3-3c that the number concentration increased with decreasing particle size (MesoPs 0.08 items/m^3 < LMPs 1.62 items/m^3 < SMPs 8,120 items/m^3), whilst the mass concentration decreased (MesoPs 1280 µg/m^3 > LMPs 460 µg/m^3 > SMPs 60 µg/m^3). In terms of the size composition, particles smaller than 40 µm and 100 µm respectively occupied half and 95% of the total number of plastic debris, while SMPs in total occupied over 99.94% (Figure 3-3b). On the other hand, 96% of the total mass of plastics comprised of particles >1,000 µm in which MesoPs occupied 64% (Figure 3-3d). Interestingly, particles around the upper size limit of MPs (5,000 µm) covered almost one-fifth of the total mass. The proportions shared by LMP and SMP were 34% and 2% respectively.

Both number and mass concentrations of MPFs displayed skewed normal distributions with respect to fiber lengths (minimum length = 18 µm; maximum length= 4,800 µm; average diameter: 24 µm) (Figure 3-4a and Figure 3-4c). The peak number and mass concentrations were noted at 100–200 µm (640 items/m^3) and 1,000–2,000 µm (220 µg/m^3) length ranges, respectively. Overall, MPFs smaller than 1,000 µm in length occupied 86% (with 51% less than 300 µm) in terms of number, and 54% in terms of mass (Figure 3-4b and Figure 3-4d).

Figure 3-5a and Figure 3-5b indicate the ratio between plastic particles and MPFs in terms of number and mass, respectively. The number proportion of particles dominated over MPFs in the 10–100 µm size category, but with increasing size, the share of MPFs significantly increased, marking >98% for particles larger than 300 µm (Figure 3-5a). The mass-based distribution showed a similar tendency, where MPFs were predominant over particles between 100–3,000 µm (Figure 3-5b). The maximum MPFs proportions compared to particles were noted around 300 µm.

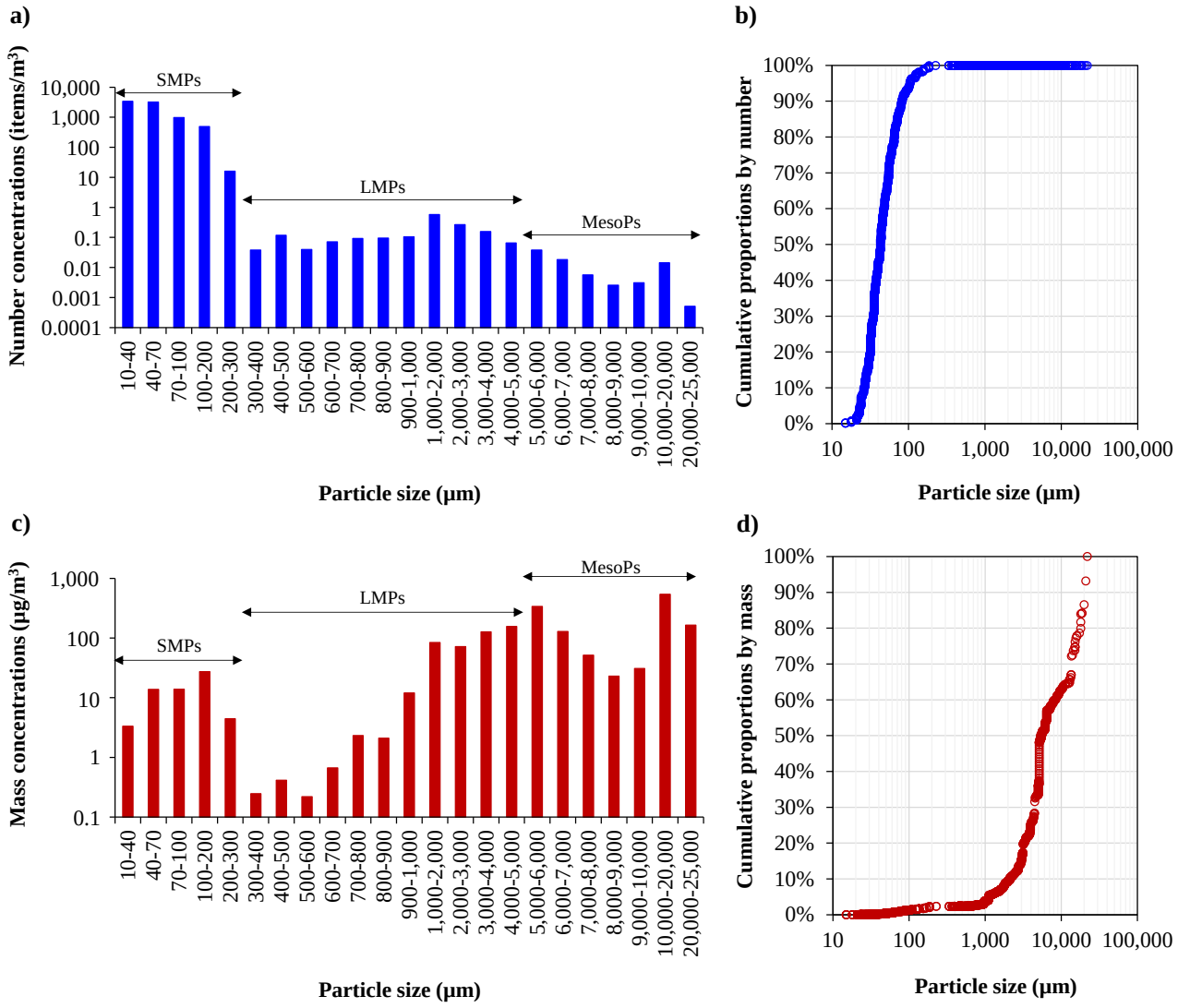


Figure 3-3 Size distributions of plastic particles based on number and mass concentrations (Variation of a) number concentrations of plastics and b) cumulative proportions of the number of plastics, with particle size; Variation of c) mass concentrations of plastics and d) cumulative proportions of the mass of plastics, with particle size).

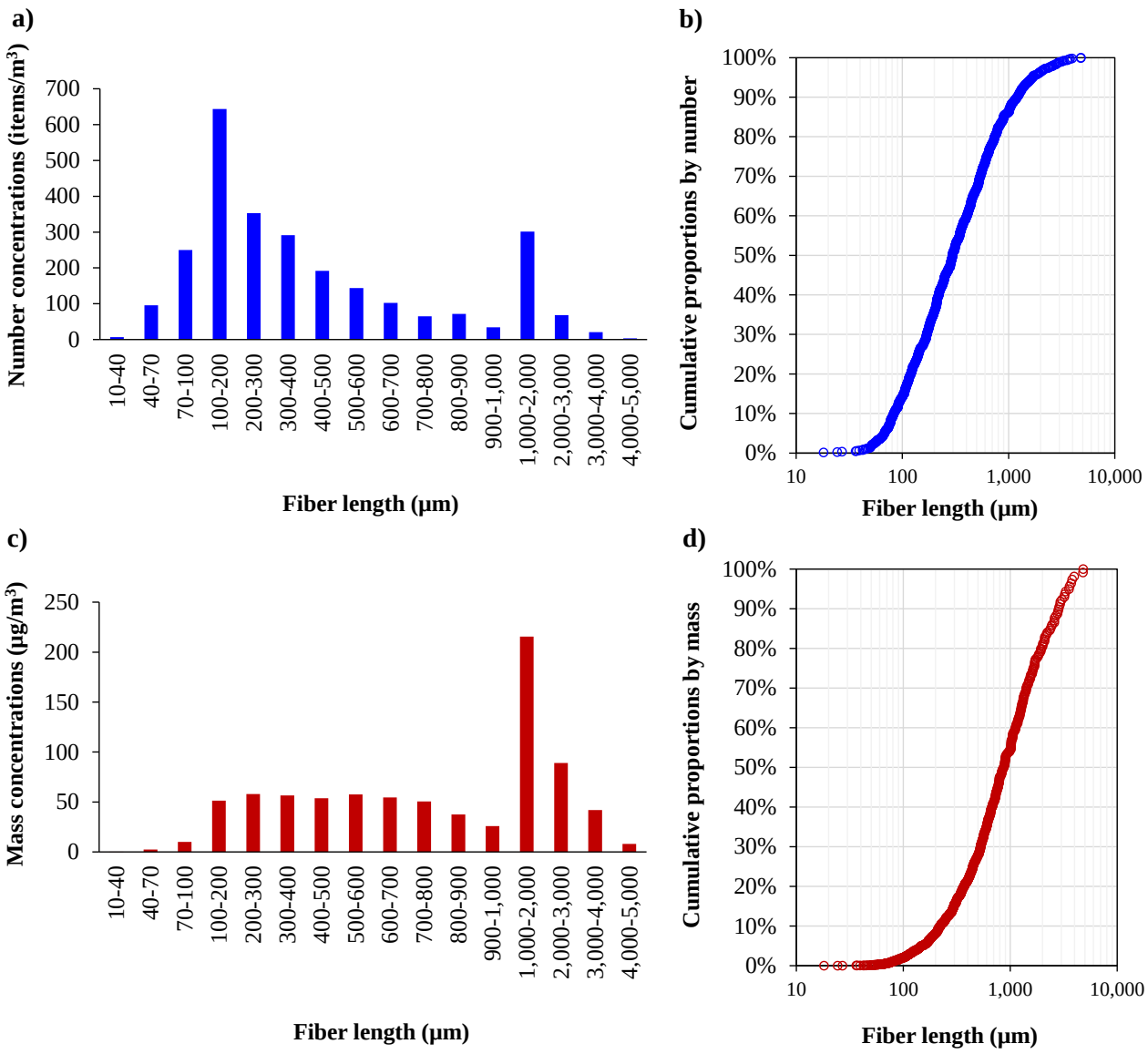


Figure 3-4 Size distributions of MPFs based on number and mass concentrations (Variation of a) number concentration of MPFs and b) cumulative proportions of the number of MPFs, with fiber length; Variation of c) mass concentration of MPFs and d) cumulative proportions of the mass of MPFs, with fiber length; "MPFs" refers to microplastic fibers)

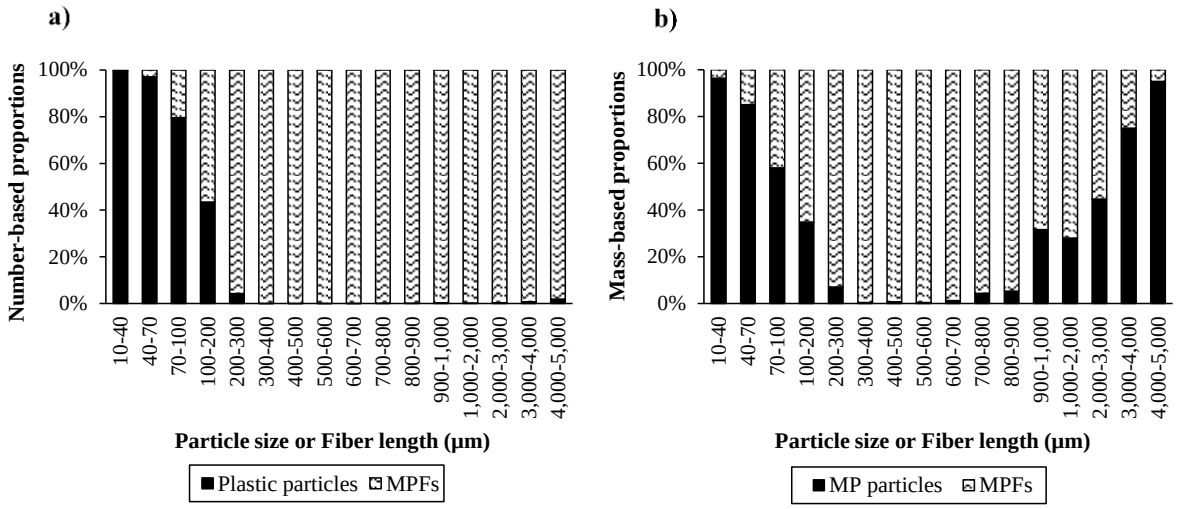


Figure 3-5 The proportions of plastic particles to MPFs
a) in terms of number, and b) in terms of mass ("MPFs" refers to microplastic fibers)

3.3.3 Physical and chemical characteristics of plastics

The polymer composition of plastic particles detected in the study area is shown in Figure 3-6a (based on number) and Figure 3-6b (based on mass). Additionally, the color and shape distributions of plastic particles are shown in Figure A–1. The polymer composition based on the number was rather homogeneous throughout the river network, whilst the same based on mass depicted a varying composition on account of the differences in polymer densities and particle sizes (Figure 3-6a and Figure 3-6b). In general, polyethylene (PE) (59% by number; 45% by mass) followed by polypropylene (PP) (23% by number; 21% by mass) were dominant in most of the locations. Polyethylene terephthalate (PET, 76%) and ethylene propylene diene monomer (EPDM; 70%) shared the major proportion in terms of the mass at R2 and R3, respectively. Other common polymer types included polystyrene (PS), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), and styrene-butadiene rubber (SBR). Polymers like PVC, PMMA, EPDM, and SBR were absent in the midstream, despite their significant presence in the upstream. The existing studies on riverine MPs presented scarce evidence on the particle size distribution of different polymer types. In the present case, PE and SBR extended over a wide size range while other polymers clustered within shorter size spans (Figure 3-6c). PE, PVA, and some other trivial polymer types were abundant among SMPs (median: ~100 µm), whereas PET and PVC were common in the range of MesoPs (median: ~5,000 µm).

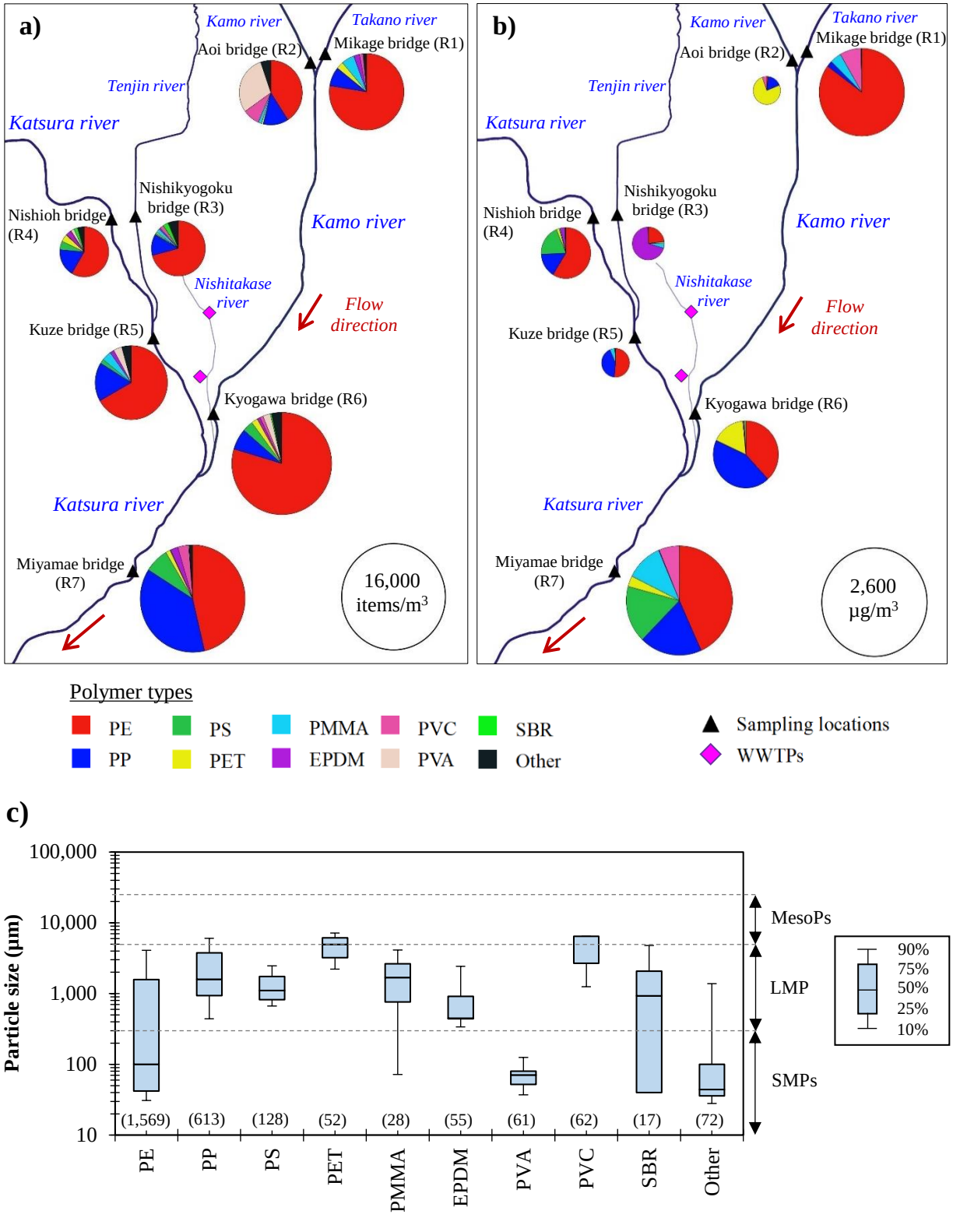


Figure 3-6 Distribution of polymer types along the river network
a) polymer distribution by number, and b) polymer distribution by mass (the mass concentration at R7 is five times the magnitude shown by the area of the pie chart); c) particle size distribution of different polymer types

Moreover, the mean particle sizes of PVA, PET, and PVC were significantly different compared to those of other polymer types (p<0.05). The remaining polymers were frequent in LMPs, with a median size of ~1,000 µm. PS was mainly found as fragments and spheres whereas PET was mostly spotted as clusters of fibers. Based on the color of the fluorescent MPFs, PET/Nylon-like fibers (44% by number; 46% by mass), and acrylic-like fibers (43% by number; 46% by mass) were found to be equally dominant in the watershed, with a small proportion of PP/PE-like fibers (Table A4 and Figure A–2). The polymer composition did not vary significantly upon fiber length (Figure A–2).

3.4 Discussion

3.4.1 Plastic contamination levels in Japan and comparison to global rivers

This study demonstrated that plastic pollution is widespread in a small urban river network in Japan, indicating the total concentrations ranging between 3,550–15,840 items/m^3 (180–13,180 µg/m^3) for microplastic particles, and 1,470–3,600 items/m^3 (520–1,060 µg/m^3) for microplastic fibers. Urbanization has been recognized as a crucial factor affecting plastic pollution in aquatic environments, and increasing proximity to densely urbanized areas has been found to increase MP concentrations in the rivers (Mani et al., 2015; Yonkos et al., 2014). In agreement, our results indicated gradually increasing abundances of plastics towards the downstream of the river network, as the flow progressed through swiftly changing land use patterns from forest patches in the upper reaches to heavily built-up areas in the downstream. However, certain upstream stations in the river network (e.g., R1) showed relatively high plastic concentrations, possibly due to intensive human activities associated with the riverbanks and the stormwater outlets located therein (Boni et al., 2022; Kataoka et al., 2019; Shruti et al., 2022). The exceptionally low concentrations in the midstream could be explained by the wider flood plains and the very low flow conditions (specially at R5), as they allow the trapping of some plastics in the flood plains and promote the sinking of heavier plastic particles along the water column (Ding et al., 2019; Lechthaler et al., 2021).

Between midstream and downstream, the two WWTPs of the city are releasing treated effluent into the Katsura River, and the Kamo River (through Nishitakase River). The total volume of treated effluent accounted for approximately 38% of the downstream river flow, and 28% of the MP number loads (3% of MP mass) passing through the river

network within a dry day (refer to Text A–2). Additionally, the downstream of Katsura River encompasses a vast area of agricultural lands, potentially releasing a significant volume of agricultural runoff. Moreover, several small-scale tributaries and canals are connecting to the Katsura River as it reaches downstream with increasing channel cross section and discharge (Table A–1). These factors may give rise to the maximum concentrations in the downstream (Hitchcock, 2020; M. Liu et al., 2018; Murphy et al., 2016; Wong et al., 2020).

Although WWTP effluent is considered a significant source of MPFs in rivers, a clear relationship was not derived between the concentrations of MPFs and the spatial distribution of WWTPs in the present study. The amount of MPFs detected in surface water can be affected due to the role played by turbidity currents in retaining fibers within the river sediments (Pohl et al., 2020). Concurrently, WWTPs could contribute to MPFs, compensating for those retained in sediments. The higher MPF levels observed along the Kamo River than the Katsura River in this study can be ascribed to the involvement of human activities which lead to fiber inputs via surface runoff and atmospheric depositions of textile fibers (Dris et al., 2016, 2018).

Utilizing the most appropriate sampling methods for different size clusters of plastic particles spanning over a wide range, we showed that the number concentration of SMPs would be 10^3–10^4 times that of LMPs, and LMPs would be about ten times the concentration of MesoPs in the surface water of a typical urban river (Figure 3-3a). Consistent with previous studies, our findings indicated that plastic particles smaller than 300 µm in diameter are more pervasive in river water (Eo et al., 2019; Han et al., 2020; Mintenig et al., 2020; Mughini-Gras et al., 2021), and occupies over 99% of the total number of plastic debris in river water regardless of their insignificant mass. MesoPs are small in number yet could lead to a larger number of tiny MPs due to successive fragmentation (Cole et al., 2011). A comparable size distribution as the current study was presented by (Isobe et al., 2015) for the number concentrations of plastic particles spanning between 300 µm to >30 mm in the SJ and SIS, indicating urban rivers as a vital source of plastics in the receiving sea around Japan. Additonally, the proportion of MesoPs within the total particle size range of 300–25,000 µm was comparable to the previous reports (Table A–8). The size distribution of plastic particles indicated relatively less amount of particles around 300–1,000 µm (Figure 3-3), possibly due to the interference of mesh size of the plankton nets involved in sampling LMPs. These nets

might subject to stretching when deployed from bridges and kept in water for several hours during sampling. Subsequently, the diagonal mesh size of the plankton net is larger than 300 µm, resulting the particles around the size of the mesh to pass through the net, without being retained.

Contrasting to plastic particles, the size composition of MPFs showed a lower occupancy of the smallest MPFs (10–100 µm), possibly due to the loss of fibers through the 10 µm net used in sampling (Dris et al., 2018), it may also reflect the actual size limits of MPFs in the river under the effects of flow dynamics. On top of that, our size distribution of MPFs compares well to the same derived by Vassilenko et al. (2021) for textile fibers formed in domestic laundering, implying that the size limits are expected as MPFs originate mainly from consumer apparel. A comparable fiber distribution was also recorded for the Sein River (France), where 250–850 µm long fibers indicated the highest concentrations (Dris et al., 2018).

The present results indicated that the proportions of MPFs compared to plastic particles would be maximized around 300 µm. This could be supported by the evidence suggesting the enhanced release of textile fibers and increased ingestion by aquatic lives at the length of 300 µm (Jemec et al., 2016; Vassilenko et al., 2021; Zambrano et al., 2019). The occurrence of plastic particles was pronounced in the smaller size range (<100 µm), perhaps due to the higher fragmentation of particles, or the relatively lower presence of MPFs due to previously stated reasons. However, at larger sizes, the mass of particles surpassed that of MPFs owing to larger particle volumes. The differences in the size distributions of plastic particles and MPFs inferred that they might behave differently in the environmental matrices; thus, adopting dedicated analytical protocols for MPFs would be vital.

Figure 3-7 (supplemented with Figure A–3) compares the number concentrations of plastics found in the present study (except MPFs) with those reported from other riverine environments in the world, with respect to the minimum particle size considered in the respective studies. Figure 3-7 illustrates that the studies which included smaller particles (generally <100 µm) attained higher concentrations. This complements the explanation in Section 3.3.2, which suggests higher concentrations can be ascribed to the smaller particle fraction. Therefore, the inclusion of very small debris sizes is imperative to understand the severity of plastic pollution in a given watershed. However, different river environments, even within the same country, may indicate vastly varying

concentrations with respect to the same minimum particle size (for instance, [17] and [14] from China, Figure 3-7), owing to the disparities between catchment characteristics, proximity to urban centers, population densities, meteorological conditions, etc. (Kataoka et al., 2019; W. Wang et al., 2017; Yonkos et al., 2014). Additionally, similar concentrations estimated for different minimum particle sizes would imply that the higher the minimum debris size, the more acute the plastic pollution state is, and vice versa (e.g., [23] is more polluted than [1], Figure 3-7). Hence, minimum particle size represents a meaningful indicator for comparing the extent of plastic pollution among different watersheds.

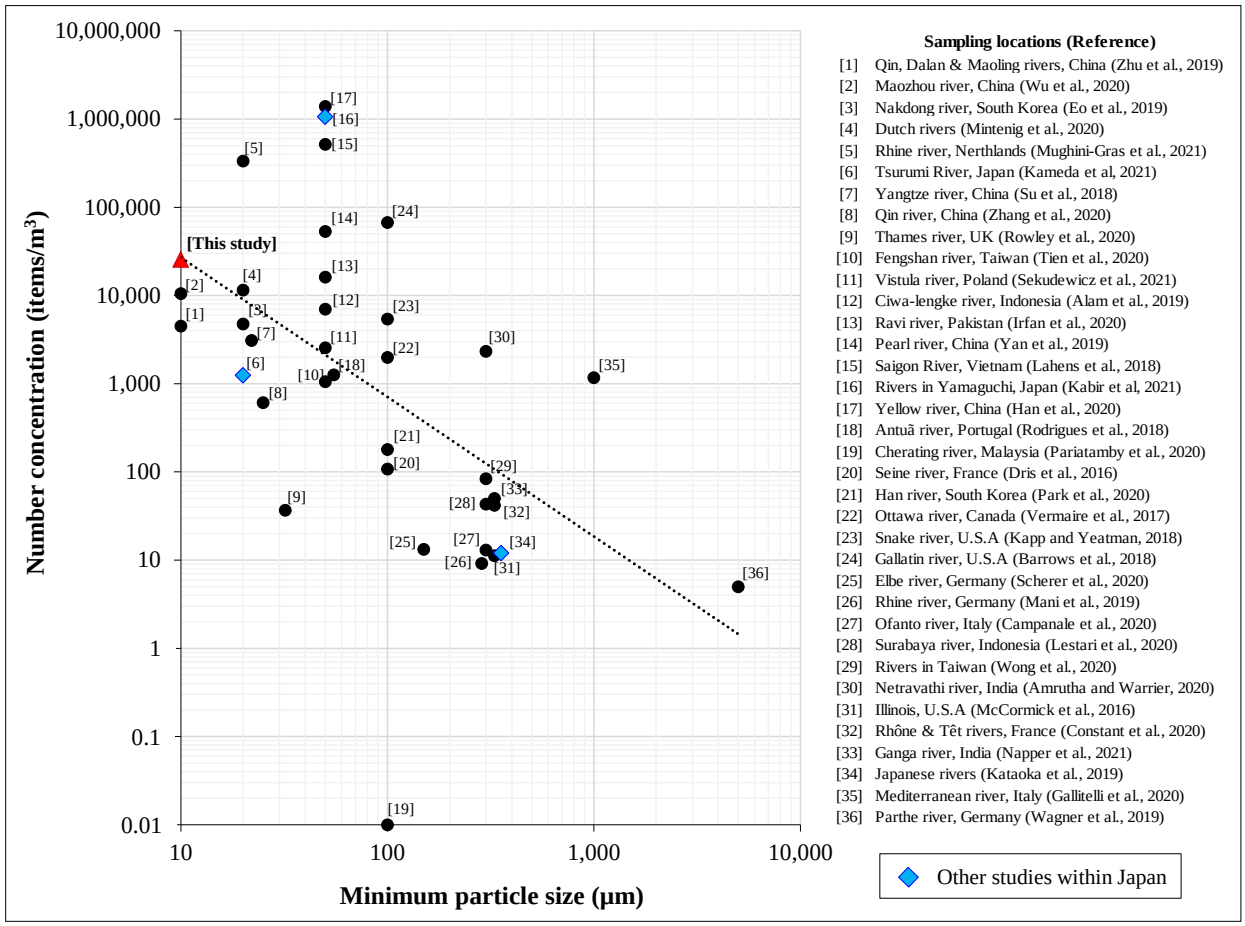


Figure 3-7 Global comparison of plastic concentrations in riverine environments (This figure is supplemented with Figure A–3, and the cited references can be found therein; "minimum particle size" refers to the smallest particle size of the respective sampling range considered in each study).

Within the size range of 10–25,000 µm, the globally reported plastic concentrations largely varied between 0.01 items/m^3 to 1.4 million items/m^3. Among the studies that analyzed particles smaller than 50 µm, the present concentration was the second highest, whereas the Rhine River (Netherlands) possessed 13 times higher concentrations. Dutch rivers, Nakdong River (South Korea), Thames River (UK), and several Chinese rivers, including Maozhou, Qin, and Yangtze Rivers, marked two to seven hundred times lower concentrations compared to the current results for the same size class. Tsurumi River, another urban river in Japan comprised 20-fold lower concentrations, probably owing to the lower drainage area compared to the present case. Nevertheless, for MPs between 50–300 µm; the rivers in Yamaguchi, Japan, possessed some of the highest concentrations ever reported, together with the Yellow River in China. The concentrations in Yamaguchi-rivers are exceptionally high (40 times higher than the present concentrations), despite the lower basin area and population density of the respective catchments compared to those in Kyoto. Additionally, 2–54 folds higher concentrations were estimated for the Pearl River (China), Saigon River (Vietnam), and Gallatin River (USA). The global comparison in Figure A–3 also includes LMPs, and MesoPs. While only a limited number of studies exclusively reported on MesoPs in river water, more data on such larger particles is mandatory to elucidate whether their emissions into rivers are linked with plastic waste mismanagement.

The MPFs concentrations found in the rivers of Kyoto City (2,640 ± 800 items/m^3) were very low compared to the fiber concentrations found in the highly polluted Saigon River, Vietnam (Lahens et al., 2018). In this river, the concentrations of anthropogenic fibers were as high as 172,000–519,000 items/m^3, of which 92% were of synthetic origin; and the absence of WWTPs to treat domestic and industrial effluents, and the presence of the textile and apparel industry in the surrounding vicinity were recognized as potential reasons for such high fiber concentrations (Lahens et al., 2018). Much lower concentrations than the present study were found in the Hudson River, United States (Average: 985 items/m^3) (R. Z. Miller et al., 2017); and Seine River, France (4–108 fibers/m^3) (Dris et al., 2018), where wastewater was properly managed through WWTPs similar to the present case.

3.4.2 Occurrence by polymer types and the potential sources

Plenty of research, including the present study documented PE and PP as the most frequently occurring MP polymer types in rivers (Campanale et al., 2020; Lahens et al., 2018; Lin et al., 2018; Mintenig et al., 2020; Rodrigues et al., 2018). This is primarily owing to their extensive production and wide applications worldwide (Plastic Europe, 2022b). These two polymers accounted for 47% of the total polymer production in 2021 in Japan which is consistent with our observations (Japan Plastics Industry Federation, 2022; Plastic Europe, 2022). Additionally, PE and PP are easily mobilized in the water while weathering into smaller fragments due to their low density (0.91–0.97 g/cm^3) (C. Wang et al., 2020). Although PE and PP are detected at equally high abundances in aquatic environments worldwide, the present findings implied that PE might be more susceptible to fragmentation compared to PP (p<0.05) as attested by its ubiquity in the SMPs range (Figure 3-6c).

The high proportions of PS in river water were likely originated from its extensive applications in food packaging at the convenient stores and supermarkets in Japan. Moreover, it is widely used in construction and automotive industries (Plastic Europe, 2022). PET on the other hand, were probably derived from clothing and packaging. Construction, and electronics industries which are active in metropolitan Kyoto, could be the likely sources of PVC (Plastic Europe, 2022). PVA has not been frequently reported as a dominant polymer type in global riverine studies; nonetheless, Kabir et al., (2021) also reported that PVA-type polymers are pervasive in the sub-urban rivers of Japan. Lastly, the presence of PMMA, EPDM, and SBR suggested the inflows of road and tire wear particles through surface runoff (Yukioka et al., 2020). As explained in Section 3.4.1, the midstream may act as a sink for heavier plastic particles, given their high densities, which can be an explanation for the reduction in PVC (1.40 g/cm^3) and PMMA (1.18 g/cm^3). Conversely, the shallow water depths in the upstream stations (R2 and R3) resulted in the retrieval of large proportions of high-density polymers like PVC, PVA (1.40 g/cm^3), and PET (1.38 g/cm).

With regards to MPFs, the previous studies cited higher proportions of fibers in river water compared to the other shapes of MPs (Constant et al., 2020; Lenaker et al., 2019; Luo et al., 2019; Napper et al., 2021; Sekudewicz et al., 2021; L. Zhang, Liu, et al., 2020; G. Zhou et al., 2020). In the present study, MP-fibers were not successfully detected in the size range of SMPs with μ-FTIR. This further manifest the importance of adopting

dedicated protocols for analyzing MPFs rather than the conventional methods in practice. The methodologies employed in sampling, processing, and characterizing MPs could result in a considerable loss of fibers, thus may underestimate the actual number of fibers in a sample. Sampling of LMPs using plankton nets (300 µm mesh size) may allow fibers to pass through the nets in the longitudinal direction; hence, low mesh sizes are ideal for sampling MPFs as in the present study (Dris et al., 2018; Rebelein et al., 2021). The existing research widely used microscopes to detect MPFs, poorly differentiating between plastic fibers and natural fibers, and hardly spotting transparent MPFs (Rebelein et al., 2021). These issues were partly addressed in the current study with the use of NR staining, which exempted natural fibers from appearing with fluorescence (Shruti et al., 2022). Furthermore, it permitted a quick assessment of the potential polymer types of MPFs, which is a viable alternative when precise polymer characterization is not obligatory.

The dominant polymer types of MPFs observed in the present study (PET/Nylon and acrylic-like MPFs) are extensively utilized in the production of fabrics for apparel and other finished textile goods (Carr, 2017). Kabir et al. (2021) ascribed the occurrence of MPFs in the rivers in Yamaguchi (Japan) to point-sources like domestic sewage, laundry drainage, WWTP effluents, discharges from apparel industries, and non-point sources like fishing activities, and various urban and agricultural sources. The public sewage network coverage of Kyoto City is nearly 100%; thus, fiber inputs from domestic septic systems and industrial discharges would be insignificant in the present case (JSWA, 2021). Since fishing activities do not take place commercially in the study area, urban and agricultural runoff, atmospheric depositions, and WWTP effluents may represent the dominant sources of MPFs in the rivers of Kyoto City (Browne et al., 2011; Dris et al., 2016; Napper & Thompson, 2016).

3.4.3 Load and fate of plastic being transported by the rivers in Kyoto

The daily loads of MPs, MesoPs, and MPFs conveyed to the Yodo River through the Katsura River during a typical dry day were calculated using the number/mass concentrations and the discharge of the river network (Table 3-2). It should be noted that the concentrations may vary based on the vertical and lateral profiles of the river. As per the estimations, 29 billion SMP, 30 million LMP, and a million MesoP particles are carried away with the surface water of the Katsura River within a day. In terms of mass, the daily loads were 0.1 kg, 9.0 kg, and 15.3 kg for SMPs, LMPs, and MesoPs,

respectively. Overall, the Kamo and Katsura Rivers seem to contribute equally to the plastic pollution downstream of the river network (Table 3-3).

Table 3-2 Plastic loads conveyed through the river network

Sampling station	Load based on number (items/day)				Load based on mass (g/day)			
	MesoPs	**LMPs**	**SMPs**	**MPFs**	**MesoPs**	**LMPs**	**SMPs**	**MPFs**
Mikage bridge	1.78×10^{4}	1.67×10^{5}	1.38×10^{9}	5.13×10^{8}	237	40	7	144
Aoi bridge	1.52×10^{3}	5.75×10^{4}	6.79×10^{8}	1.69×10^{8}	7	9	5	60
Nishikyogoku bridge	3.81×10^{2}	8.03×10^{3}	1.73×10^{8}	7.75×10^{7}	7	2	1	29
Nishioh bridge	1.15×10^{4}	1.23×10^{6}	3.12×10^{9}	1.98×10^{9}	53	395	61	825
Kuze bridge	1.43×10^{4}	4.51×10^{5}	1.17×10^{10}	4.06×10^{9}	45	75	150	1,440
Kyogawa bridge	3.23×10^{4}	8.01×10^{5}	1.48×10^{10}	3.60×10^{9}	721	160	110	881
Miyamae bridge	9.70×10^{5}	3.03×10^{7}	2.93×10^{10}	6.40×10^{9}	15,300	9,020	74	1,960

Note: *"MesoPs" refers to mesoplastics in the size range of 5,000–25,000 µm; "LMPs" refers to large microplastics in the size range of 300–5,000 µm; "SMPs" refers to small microplastics in the size range of 10–300 µm; and MPFs" refers to microplastic fibers in the size range of 10–5,000 µm*

Our data revealed only 28% contribution to the river MP loads by number of plastic particles (3% by mass) by WWTP effluents, the major point sources within the catchment, during a typical sunny day (Text A–2). The remaining 72% is derived through non-point sources, like atmospheric deposition and the previous depositions within the river channels through runoff inflows. Additionally, the MesoPs loads downstream were extremely high compared to the upstream, implying a significant influence of the non-point sources, viz. urban and agricultural runoff. The active road network of Kyoto City traverses over the Kamo and Katsura Rivers; hence, plastic debris are supposedly conveyed to these rivers through roadside gutters and stormwater canals carrying wash water from the city. Additionally, the sweeping water from farmlands spreading across the downstream of the Katsura River can transport plastic waste from crop covering, fertilizer packaging, irrigation piping etc. Some MesoPs recovered in the present study were likely occurred from broken road cones, artificial grass, and fertilizer particles originating from the said non-point source (Figure A–4). The large quantity of SMPs transferred through the Katsura River can seriously impact the downstream ecosystems. Since Yodo River acts as the primary source of drinking water for the inhabitants of Osaka Prefecture, it is vital to control the inputs of MPs, especially SMPs (<300 µm), which are

loaded in billions per day into the Yodo River system, and Osaka Bay, the ultimate destination of the river flow.

Table 3-3 Plastic loads conveyed to Yodo River from Katsura river (at Miyamae bridge)

	MesoPs	**LMPs**	**SMPs**	**MPFs**
Items/day	1 million	30 million	29 billion	6 billion
kg/day	15.3	9.0	0.1	2.0
Contribution to the loads from upstream of the Katsura River	1.5%	1.5%	40%	63%
Contribution to the loads from upstream of the Kamo River	3.3%	2.6%	51%	56%

Note: *"MesoPs" refers to mesoplastics in the size range of 5,000–25,000 µm; "LMPs" refers to large microplastics in the size range of 300–5,000 µm; "SMPs" refers to small microplastics in the size range of 10–300 µm; and MPFs" refers to microplastic fibers in the size range of 10–5,000 µm*

The total load of MPFs transported to the Yodo River was estimated at 6 billion fibers per day and 2.0 kg per day. MPFs can be more toxic to aquatic life than other shapes of MPs (Gray et al., 2017), yet controlling their environmental emissions is arduous. The comparison of river-MPF data between countries (Section 3.4.1) portrayed that well-planned sewage networks, together with WWTPs, control MPF emissions into rivers to a greater extent, although WWTP-effluents can still release some amount of MPFs along with treated effluent. Comparison of the characteristics of MPFs in river water with those in air, soil, stormwater, and WWTP effluent would be useful in verifying the likely sources of MPFs, which should be an area of interest for future research.

3.5 Conclusions

This study denoted the first attempts to elucidate the effects of particle size on the occurrence and distribution of plastic debris in an urban river network, based on a wide size range of particles (10–25,00 µm). The urban river network of Kyoto (Japan), comprising the Kamo and Katsura Rivers, was investigated for this purpose, where moderate plastic concentrations were attained compared to the levels reported worldwide and within Japan. We added to the current knowledge that plastic abundances in urban river networks may gradually increase as the flow progresses towards the built-up areas, while acting as sinks for denser plastics. Urban discharges of non-point origin seem to

contribute to over 70% of the river MP budget during dry days. Our findings depicted that the total number of plastics occupied 99.94% SMPs (but only 2% in terms of mass), including 50% less than 40 µm. In terms of the mass, 96% comprised debris larger than 1,000 µm, including 64% MesoPs. Interestingly, the particles around 5,000 µm solely occupied 20% of the total mass. PE fragments were dominant in the river water, especially within SMPs, implying their high tendency to fragmentation compared to PP and other polymer types. Additionally, PVA exclusively occurred in the SMPs range. We emphasized that the inclusion of smaller particle sizes would be vital in elucidating the severity of plastic pollution in a watershed.

Furthermore, this work provided insights on developing a dedicated method for the analysis of MPFs, such as fluorescence-tagging, over the conventional methods of analyzing MPs. MPFs were found to be primarily sourced from consumer textiles and apparel, where they were predominant over MP particles between 100–3,000 µm. The peak occupancy of MPFs was noted at 300 µm (>98%), clarifying why this size can be alarming to the existence of aquatic life. Ultimately, the present findings would be useful in understanding the entirety of plastic pollution in an urban river network and formulating strategies to control plastic emissions into fluvial environments in the future.

CHAPTER 4. Inter-event and intra-event dynamics of microplastic emissions in an urban river during rainfall episodes

4.1 Introduction

The unprecedented growth in plastic production and indiscriminate disposal of wastes debilitate the current efforts to control plastic pollution globally (Borrelle et al., 2020). The mismanaged plastic waste may end up in various locations in the environment, weathering into smaller pieces that are commonly known as microplastics (1 µm – 5 mm in size) (Frias et al., 2019). In 2015, 0.8 million tonnes of mismanaged plastic waste entered the global rivers, affecting nearly 84% of the rivers by surface area (Nyberg et al., 2023). This is a serious concern, given that rivers represent the major conduits transferring plastic debris, including tiny microplastics, from land to the oceans (Meijer et al., 2021). Urban agglomerations are regarded as hotspots of microplastic pollution, with urban rivers acting as the key receptors of those microplastics via both point sources, and non-point sources (Kataoka et al., 2019). The contribution of point sources, primarily wastewater treatment plants (WWTPs), to the microplastic contamination of rivers has been widely investigated (Carr, 2017; Ziajahromi, Neale, et al., 2017). Nevertheless, there is scarce information on the impacts of non-point sources, particularly surface runoff of rainfall events, on the dynamics and real-time concentrations of microplastics in rivers, while numerous inorganic and biological non-point source pollutants have indicated characteristic emission patterns during such events (Dong et al., 2021; Xie et al., 2019).

The recent research emphasized surface runoff as a crucial source of microplastics, portraying a greater contribution to microplastic pollution compared to the point sources (Cho et al., 2023; Treilles et al., 2021; Yano et al., 2021). Microplastic (20–100 µm) levels as high as 8,580 particles/L have been detected in the urban runoff samples collected from various parts of the world (C. Wang et al., 2022). Additionally, the temporal dynamics of the abundances and characteristics of microplastics have been investigated in a few recent studies (Cho et al., 2023; Sun et al., 2023). In terms of the effects of runoff on the receiving water bodies, significant fluxes in microplastic abundances in both freshwater and marine environments have been reported after rainfall events, storms, floods, and typhoons (Gündoğdu et al., 2018; Hitchcock, 2020; Hurley et al., 2018). A majority of the studies estimated a higher contribution to the annual emissions of microplastics by wet or

monsoon season than by dry season (Cheung et al., 2016; Eo et al., 2019; Veerasingam et al., 2016). Additionally, regression-based correlations have been proposed between rainfall characteristics and microplastic abundances (Hitchcock, 2020; T. Liu et al., 2020; Wong et al., 2020; W. Xia et al., 2020).

These findings added strong evidence to the central role that rainfall episodes and subsequent runoff play in aggravating the microplastic pollution of aquatic environments. However, they provided little knowledge of the temporal effects of microplastic mobilization in rivers during the onset of rain. While most of the studies sampled in lentic water environments like lakes, reservoirs, and bays, that are hardly as dynamic as rivers, the handful of studies focusing on rivers sampled at an insufficient frequency to capture the real-time dynamics of microplastic emissions. The time resolutions of sampling involved only a few times during the dry and wet seasons (Lima et al., 2014; Rodrigues et al., 2018), before and after extreme rainfall episodes (Cheung et al., 2016; Hurley et al., 2018), and daily or intermittent sampling during rainfall events (Hitchcock, 2020; Wong et al., 2020). The lack of studies with rigorous sampling designs can be ascribed to the uncertainties and challenges encountered in sampling manually during rain.

Furthermore, the existing studies presented scant information on the effects of particle size on the real-time discharges of microplastics during rain. It is prudent to clarify those details because microplastics of varying particle sizes would be differently affected during the build-up and wash-off processes (Morgan et al., 2017), and the complex fluvial processes in rivers (F. Xia et al., 2023). Such information would also be useful in determining the target particle sizes to eliminate for optimum pollution control of rivers. At the same time, these studies have not given enough attention to the fiber fraction of microplastics (hereinafter referred to as “MPFs”), the most ubiquitous form of microplastics in the natural environment (Browne et al., 2011). As MPFs are known to interfere with aquatic lives to a broader extent (Ziajahromi, Kumar, et al., 2017), and are poorly removed via WWTP processes (Ben-David et al., 2021), it is worth clarifying how the presence and mobilization of MPFs in rivers would be affected by rainfall events.

To bridge the aforementioned gaps in the existing research, the present study sampled microplastic particles (hereinafter referred to as “MPs”) and MPFs down to 10 µm in the surface water of an urban river in the metropolitan Kyoto, Japan, during three rainfall events with varying characteristics. Sampling was conducted at a high frequency over the entire course of the target rainfall events, for the first time in riverine microplastic

research. The specific objectives of the study include,

1. to elucidate the effects of rainfall characteristics on the inter-event and intra-event dynamics of various size clusters of MP and MPF emissions,
2. to investigate rainfall-driven changes in the quantities and characteristics of MPs and MPFs compared to the dry weather, and finally,
3. to discuss the implications for microplastic pollution control of rivers during rain.

This study may enlighten future research on investigating the integrated impacts of rainfall and subsequent runoff on the dynamics of microplastic pollution in rivers and formulating mitigation measures for such pollution at the catchment scale. Appendix B provides the supplementary information relevant to this study which shall be referred to in conjunction with Chapter 4.

4.2 Materials and methods

4.2.1 Study area

The study area comprised a sub-catchment of the primary river network of Kyoto City, Japan, representing a perfect example of an urban catchment. On all occasions, sampling was conducted at the Mikage bridge of Takano River (35° 2' 3.37" N, 135° 46' 28.67" E) (Figure 4-1). Originating in the north part of the Sakyo ward of Kyoto, the Takano River (17 km long) flows towards the south to merge with the Kamo River, one of the two major Rivers of metropolitan Kyoto. The discharge of the baseflow of Takano River at the sampling location is 4.75 m^3/s (Shivakoti, 2007). The land use of the far upstream comprised forests and grasslands, and it swiftly changed to built-up areas towards the downstream, where sampling was conducted. With a population density of 1,782 persons/km^2 (Kyoto City, 2020), this area is famous as an academic hub, a cultural hotspot, and a key tourist destination in Japan; therefore, the river is quite popular among both locals and tourists for various types of recreational activities. The study area is connected with separate sewers, providing coverage of 99.5% (JSWA, 2021). It facilitates the separate conveyance of the sewage and industrial wastewater into two WWTPs, and the surface runoff into the river via a stormwater drainage network.

4.2.2 Sampling

The sampling involved three rainfall events with different characteristics (Table 4-1), which occurred between October 2021 and April 2022. The three events were termed Event 1 (6 mm rainfall lasted for 5 h), Event 2 (24 mm rainfall lasted for 7 hours), and Event 3 (52 mm storm event lasted for 7 hours), considering the order of their occurrence. Depending on the maximum rainfall intensity (Table 4-1), Events 1, 2 and 3 were classified as light (<2.5 mm/h), moderate (2.5–7.6 mm/h) and heavy (>7.6 mm/h) rainfall events, respectively (AMS, 2012). To capture the absolute impact of runoff inflows on microplastic emissions in the river, sampling was commenced before the beginning of the rain (first sample) and continued until the river returned to a steady state after the termination of the rain (last sample). Sampling during the rain was performed at hourly intervals, but afterward, the intervals were decided based on the predicted precipitation and field conditions. In total, 10, 13, and 16 samples were collected during Events 1, 2, and 3, respectively, depending on the total duration of each event. For a comparative analysis, two additional samples were collected at the same location during two dry days in August and October 2021.

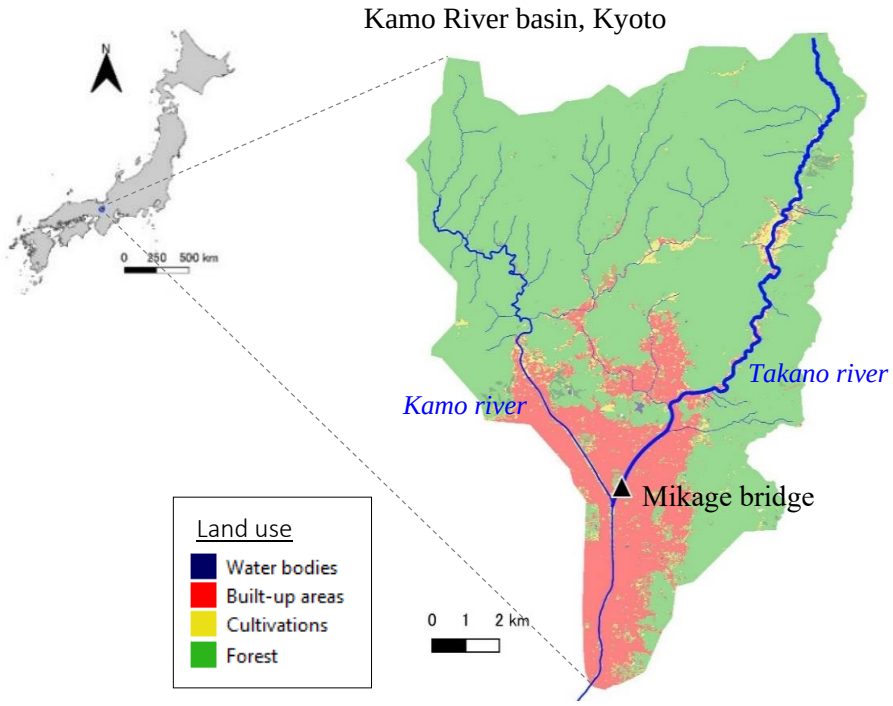


Figure 4-1 Study area and sampling site in the metropolitan Kyoto

Site sampling for 10–300 µm small microplastic particles (SMPs), and >300 µm large microplastic particles (LMPs) were performed by in-situ pump filtration, using two separate submersible pumps operated at constant speed. Water was pumped from the top surface of the river and passed through 10 µm and 300 µm plankton nets to collect SMPs and LMPs, respectively. The volume of water filtered per sample varied based on the turbidity levels and flow conditions during all three events. Simultaneously, microplastic fibers (MPFs) of 10–5,000 µm were sampled manually using a stainless-steel bucket. For each sample, 6–20 L of water was fetched and passed through a plankton net of 10 µm mesh size. In the end, all sampling nets were carefully transferred to re-sealable bags and transferred to the laboratory for analysis of MPs and MPFs. The hourly precipitation, river water level, and in-situ water quality were also recorded in parallel to sampling. Additionally, 2 L of river water was collected for the analysis of suspended solids in accordance with the standard method (APHA, 2012).

Table 4-1 Characteristics of the three rainfall events

	Event 1 (Light rainfall)	**Event 2 (Moderate rainfall)**	**Event 3 (Heavy rainfall)**
Date and time of the event	2021/10/16 04:00–09:00	2021/11/09 01:00–08:00	2022/04/29 10:00–17:00
Total precipitation (mm)	6	24	52
Duration of rainfall (hours)	5	7	7
Rainfall intensity			
Maximum (mm/h)	2.0	7.5	17.4
Average (mm/h)	0.3	3.4	7.4
Total river flow (m^3)	193,600	404,900	1,052,500
Number of antecedent dry days	3 days	14 days	2 days

4.2.3 Extraction and characterization of MPs and MPFs

The methods of extraction and characterization of MPs were similar to the protocols followed in freshwater MP research (Rodrigues et al., 2018). The samples collected into the plankton nets were carefully transferred to pre-rinsed glass bottles (1 L), using ~200 mL of 30% H_2O_2. For the removal of organic matter, wet peroxidation was performed by adding 5 mL of 0.05 M $FeSO_4$ to the solution in H_2O_2, and oven dried at 55 ℃ (wet peroxidation) for a few days. Subsequently, density separation was performed using 5.3 M NaI (1.53 g/cm^3) to remove the sediments and other inorganic constituents.

LMPs were recovered from the surface of the NaI solution by vacuum filtration of the supernatant through a 10 µm nylon net. For extraction of SMPs, the density separation process was repeated twice under centrifugation, and the supernatant was vacuum filtered through a 0.45 µm polycarbonate membrane filter. The filtrate was suspended in 50–100 mL of Ethanol (95.1–96.9 vol%) until analysis.

The size, shape, and color of LMPs were observed with a stereoscopic microscope (SMZ-161 Series, Shimadzu, Japan), while the polymer types were detected with Fourier Transform Infrared Spectrometer (Cary 630 FTIR, Agilent Technologies, USA) equipped with attenuated total reflectance (ATR), by comparing respective spectra (650–4,000 cm^{-1}) with an in-house spectral library. For each spectrum, 256 scans were performed at a resolution of 8 cm^{-1}. Only the resulting spectra with a matching degree of over 60% were taken into account after careful comparison with the respective reference spectra. SMPs were detected and quantified using a Cary 600 Series FTIR microscope (µ-FTIR). From each sample suspended in ethanol, 5 mL was filtered through a 0.2 µm inorganic membrane filter made out of alumina (Anodisc, 13 mm ∅, Whatman™, USA) for analysis. The chemical mapping was performed with µ-FTIR in transmission mode, in the wavenumber range of 4,000–900 cm^{-1}, using 16 scans performed at a resolution of 4 cm^{-1}. The obtained spectra were compared with the reference, and the polymer types were verified at a matching degree of over 85%. Depending on the morphological features, all MPs were classified as fragments, films, or spheres. Fibers were not considered in the analysis of MPs.

MPFs were isolated by fluorescence staining with Nile Red (NR) dye, following a method similar to Shim et al. (2016) with slight modifications. The samples were subjected to wet peroxidation as described for SMPs, and the digested samples were vacuum filtered through a 10 µm polycarbonate membrane filter (47 mm ∅). After that, 5 mL of 2 M HCl was applied over the filter for further removal of the remaining organic matter and lipid contents, and thereby improve the visibility of Nile Red (NR) staining. HCl was left to absorb in the filter for 5 mins and removed via vacuum filtration. Subsequently, 200 µL of 1 mg/mL NR solution (NR powder and acetone mixed at a 1:1 ratio) was added on the filter and left to absorb for 15 mins. Next, NR was also filtered out, and the PC filter was placed upside down in 20 mL of ultrapure water (Milli-Q® Reference A+ System, Millipore Corporation, USA) in a glass beaker and subjected to ultrasonication for 5 mins to transfer all the stained residues into water. This procedure was meant to avoid excess

dye binding and thereby improve the efficiency of MPF detection while avoiding overestimation. The solution in the beaker was filtered through a new 10 µm PC membrane, which was left to air-dry and covered with a clean glass slide for microscopic examination.

For analysis of MPFs, the stained filters were observed with an epifluorescence microscope (Stereozoom S9D, Leica Microsystems, Switzerland) under blue light conveyed through an orange-color high-pass filter (excitation wavelength: 485 nm, emission wavelength: >530 nm). The surface area of the filter was photographed, and only the fibers that appeared in fluorescence were manually traced with Inkscape 1.0.1 software to determine the dimensions. The polymer characteristics of MPFs were not determined in this study. However, some commercially available fibers of plastic and non-plastic origin were tested upon NR-staining to confirm the validity of the results as explained in Section 3.2.4 of Chapter 3.

4.2.4 Methods of calculations

4.2.4.1 Concentrations and loads

The concentrations of MPs and MPFs were expressed as the number of items per unit volume or mass per unit volume of water. The mass of the particles was calculated by multiplying the polymer density by the particle volume. Depending on the morphology of the particles, the volume was calculated (Equations 4-1 and 4-2) using the following criteria (Cózar et al., 2014).

$$\text{Volume of MPFs} = \pi r^2 h \quad (4\text{-}1)$$

$$\text{Volume of MPs (fragment, films, and spheres)} = 4/3\pi r^3 \alpha \quad (4\text{-}2)$$

Where "*r*" is the measured radius of each fiber, and half of the average of maximum and minimum lengths of MPs; "*h*" is the measured length of each fiber; and "α" is the shape factor (0.1 for fragments and films, and 1 for spheres).

This method of calculating mass of MPs is validated in Text A–1 (in supplementary information for Chapter 3). The calculated masses for MPs in the size range of 300 µm – 5 mm, which occupies over 94% of the total mass of MPs in the size range of 10–5,000 µm would be approximately 4 times (4.3 ± 4.5 times) higher than the measured/actual masses.

The load of MPs (and MPFs) of a given sample was calculated using Equations 4-3 and 4-4.

$$\text{Load} = CQ\Delta t \tag{4-3}$$

where, C, Q and Δt represent the concentration, flow rate, and sampling time interval, respectively. Flow rate was calculated using an empirical equation developed for the Takano River, around the sampling location (Shivakoti, 2007).

$$Q = 0.031 \times h^{1.68} \tag{4-4}$$

where h is the measured water level of the river in cm.

The total loads were calculated considering the entire time period of sampling, excluding the first and the last sample. This means, not only the duration of the rainfall, but the entire time period during which the river was impacted by the event was taken into account in the calculations. For time slots with absent data due to uneven sampling after the termination of the rainfall events, interpolation of the data between the adjacent time slots was considered.

4.2.4.2 Event mean concentrations

The event mean concentration (EMC, Equation 4-5) is employed to express the flow-weighted concentrations of MPs/MPFs for each rainfall event (Li et al., 2015), where N represents the total number of samples, and the definitions of other variables remain the same as explained above.

$$\text{EMC} = \frac{\text{Total load per event}}{\text{Total volume per event}} = \frac{\Sigma_{i=1}^{N} C_i Q_i \Delta t_i}{\Sigma_{i=1}^{N} Q_i \Delta t_i} \tag{4-5}$$

4.2.4.3 First flush coefficient

The first flush phenomenon often describes if a high proportion of non-point source pollutants is washed off during the initial part of a rainfall event. In a recent study, Sun et al. (2023) adopted this concept to describe the emissions of MPs via runoff. Geiger (1987) introduced the dimensionless *M(V)* curve that is plotted between the normalized cumulative mass of pollutants and the normalized cumulative volume of flow to analyze the first flush. In order to clarify its occurrence, the first flush coefficient (*b*), which expresses the length between the *M(V)* curve and the 45° line, is calculated by Equation

4-6, where X is the cumulative flow volume and $F(X)$ is the cumulative mass. It is considered that the experimental adjustments between $M(V)$ and $F(X)$ are acceptable, with a correlation of $R^2 > 0.9$. The first flush is said to occur when b value is less than 1, where the $M(V)$ curve lies above the identity line (Deletic, 1998).

$$F(X) = X^b \tag{4-6}$$

The details of the quality assurance and statistical analysis are documented in Section 3.2.6 of Chapter 3. Briefly, the quality assurance measures include handling the samples with stainless steel or glass utensils (except where otherwise stated), using cotton labware and laminar-flow clean bench to minimize contaminations, conducting procedural blank tests, etc. The results of blank tests are shown in Table B–1, whereas the results of recovery tests are shown in Table A–7 (Appendix A). The data were curated and processed using Microsoft Excel, while the statistical analysis was conducted using R 4.2.1. All weather information was obtained from the website of the Japan Meteorological Agency (JMA, 2022).

4.3 Results and Discussion

4.3.1 Effects of rainfall characteristics on the inter-event emissions of microplastic particles

During all three events, the river flowrate varied in sync with the rainfall, indicating maximum flow levels corresponding to the peaks in hourly rainfall (Figure 4-2a). The river flow during Events 1, 2, and 3 were 193,600 m^3, 404,900 m^3, and 1,052,500 m^3, respectively, indicating approximately 30%, 100%, and 170% increments compared to the baseflow (i.e., during dry weather). The hourly concentrations and loads of MPs fluctuated simultaneously with the river flow, except for the lagged peaks in Event 3 (Figure 4-2b and Figure 4-2c). The EMCs of Events 1, 2, and 3 were 35,000 items/m^3 (3 mg/m^3), 929,000 items/m^3 (49 mg/m^3), and 331,000 items/m^3 (33 mg/m^3), respectively (Table 4-2 and Figure - B1). The corresponding total loads were 0.5 kg (7 billion items), 19.8 kg (380 billion items), and 35.0 kg (350 billion items) for Events 1, 2, and 3, respectively (Table 4-2 and Figure B–1). The concentrations/loads of MPs at pre-rainfall and post-rainfall steady-state conditions of the river were comparable, but insignificant compared to the levels observed during the corresponding events (Figure 4-2b and Figure 4-2c).

Characterized with the smallest rainfall, Event 1 portrayed significantly lower concentrations and loads of MPs compared to the other two events (Kruskal-Wallis rank sum test, $p < 0.05$). Events 2 and 3, however, indicated comparable concentrations and loads regardless of the differences in rainfall. While the highest total loads (in terms of mass) of MPs were estimated for Event 3, the highest EMCs were noted for Event 2. Therefore, it seems that the total loads of MPs being transported are associated with the total rainfall (or average rainfall intensity of the event), while the concentrations are related to the number of antecedent dry days (ADDs) (Figure B–1). The longer ADD periods have been shown to increase the concentrations of microplastics in surface runoff due to extended accumulation on land (Cho et al., 2023; Piñon-Colin et al., 2020; Smyth et al., 2021). This clarified the higher concentrations in the receiving waters during Event 2 (11 ADDs) compared to Event 3 (2 ADDs), regardless of the difference in total rainfall (Table 4-1). On the one hand, the ADD period in Event 3 was too short to promote the accumulation of MPs (Wicke et al., 2012); and on the other hand, the preceding rainfall event might also have cleared away a sizeable proportion of MPs from the catchment, as suggested by the intensive precipitation (34 mm rainfall continued for 17 hours, with a maximum intensity of 24 mm/h).

Although the present results inferred an increase in the inter-event loads of MPs with increasing total precipitation, any empirical correlations were not derived between microplastic concentrations and the total/cumulative precipitation (Figure B–1), as shown in some previous freshwater studies which involved limited microplastic sampling during rain (Hitchcock, 2020; Wong et al., 2020; W. Xia et al., 2020). Additionally, no relationships were noted with hourly rainfall based on intra-event data. Rather, the variations in concentrations were better represented through the variations in river flow (Figure B–2). Most of the freshwater environments that discussed such correlations represented lentic environments where microplastics would rather stagnate than flow away during rain. However, the circumstances would be rather complex in lotic systems like rivers, due to the compounding hydrodynamics involved (Drummond et al., 2022). For instance, the peak emissions of MPs in Event 3 appeared with a 2-hour lag upon the termination of rainfall, suggesting resuspension of the MPs embedded in the river sediments following a storm event (Hurley et al., 2018; Niu et al., 2021). This will be further explained in Section 4.3.2.

Table 4-2 Concentrations and loads of microplastic particles (MPs) discharged during the three rainfall events

	Event	**Event 2**	**Event 3**
Number concentrations (items/m^3)			
Minimum hourly concentration	4,000	10,000	3,000
Maximum hourly concentration	87,000	3,122,000	1,460,000
Event mean concentration (EMC)	35,000	929,000	331,000
Mass concentrations (mg/m^3)			
Minimum hourly concentration	0.18	0.33	0.05
Maximum hourly concentration	10	171	120
Event mean concentration (EMC)	3	49	33
Number-based load (billion items)			
Minimum hourly load	0.09	0.18	0.04
Maximum hourly load	2	160	90
Total load of the event	7	380	350
Mass-based load (g)			
Minimum hourly load	1.5	6.1	0.6
Maximum hourly load	250	8,990	7,690
Total load of the event	510	19,760	35,000

Rainfall intensity and event duration may also affect the mobility of microplastics. Treilles et al. (2021) showed that the mobilization of microplastics occurs when the rainfall intensity exceeds 2.5 mm/h for more than 2 h. While the discharge characteristics of microplastics can be widely varied among different catchments and rainfall characteristics, our data from the lowest rainfall event inferred that an intensity of 1.5 mm/h continued for two hours would be sufficient to transfer nearly two billion MPs into the river. In the present case, the average rainfall intensities progressed over the three events (Events 1 through 3), leading to increased MP loads (Figure B–1). Additionally, the results exemplify that the effective period during which the river flow will be affected by a rainfall event should be taken into account, rather than the duration of the rainfall, to capture the full spectrum of variations in MP emissions. Implying that sampling at a high frequency would be crucial, not just during an event but also afterward, until the river returns to a steady state.

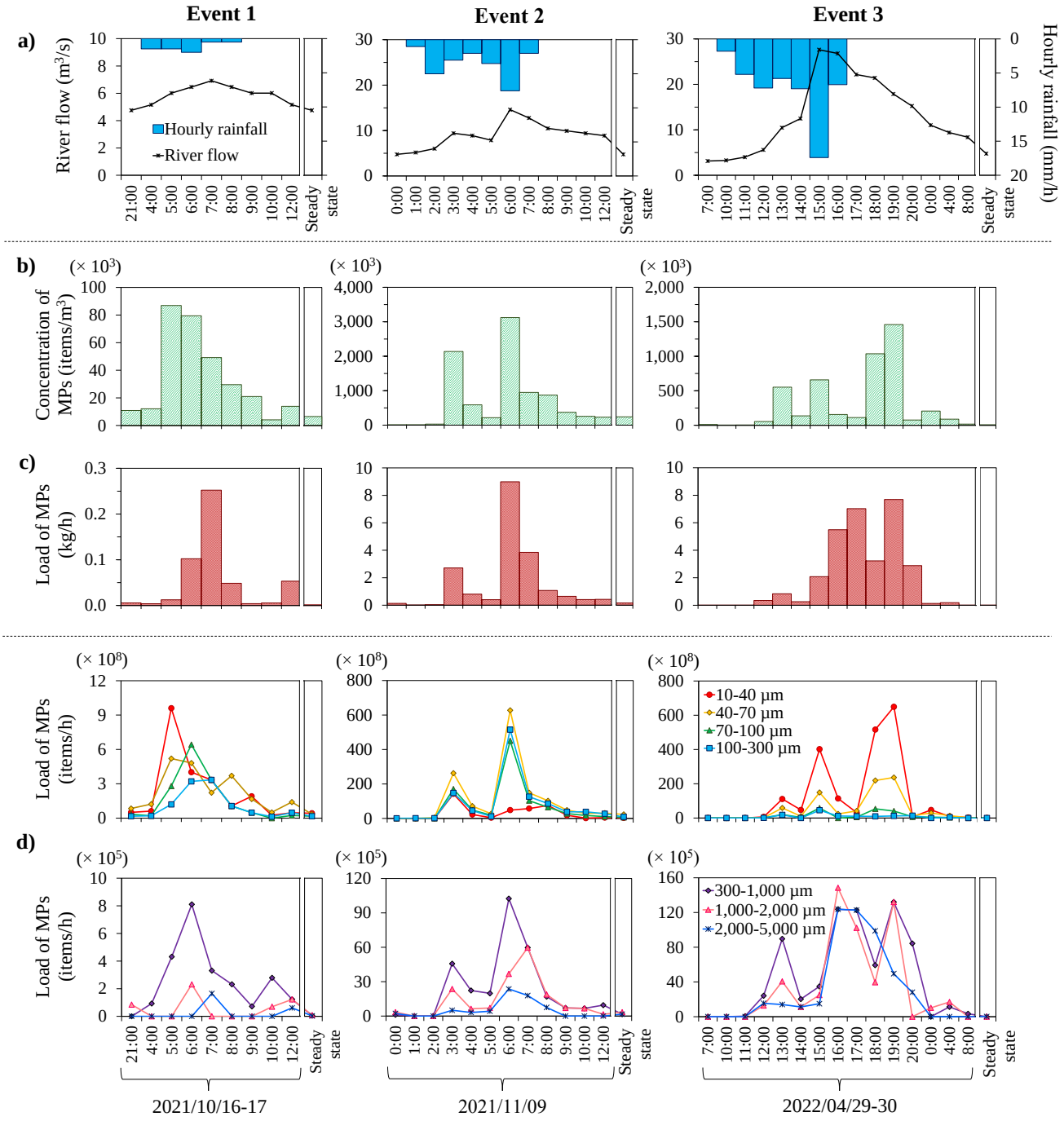


Figure 4-2 Temporal variations of microplastic emissions during rain (Variations in a) rainfall and river flow; b) number concentrations of total MPs; c) loads of total MPs in terms of mass; d) loads of MPs (in terms of number) of different size classes; In figure (a), all left *y*-axes represent the river flow in m^3/s, while the right *y*-axes denote the hourly rainfall in mm/h).

4.3.2 Synergistic effects of particle size and rainfall characteristics on intra-event emissions of microplastic particles

We discuss emissions of MPs in terms of seven size clusters as shown in Figure 4-2d. The hourly loads of SMPs (10–300 μm) were three to four orders of magnitude larger than the hourly loads of LMPs (300–5,000 μm) in all three events, and the loads decreased with the increasing particle size. The size composition of MPs may vary with time during the events, due to the size-dependent emissions of particles.

The dynamic plot of Event 1 confirms that the smallest MPs (10–40 μm) undergo the fastest and the highest emissions during light rainfalls, reaching the maximum load prior to the peak rainfall (Figure 4-2d). The emissions of larger MPs followed a sequential pattern, and the largest MPs (> 2,000 μm) are released immediately after the peak rainfall. However, moderate-intensity rainfalls (typified by Event 2) instigate a predominant emission of medium-sized MPs (40–300 μm). Nevertheless, the smallest MPs peaked at the earliest (first peak), whereas all MPs larger than 40 μm peaked around the maximum rainfall intensity. As for heavy rainfalls (e.g., Event 3), such an event incurs rather distinct emission patterns due to the tertiary peak in MP loads that transpired following the rain, during which the highest discharges of MPs smaller than 70 μm occurred. Although the smallest MPs (10–40 μm) were the highest in load, a prominent release of MPs larger than 1,000 μm was recorded in Event 3, compared to the previous events.

In Figure 4-3, the *M(V)* curves appearing above the identity line demonstrate the effect of first flush. Overall, Events 1 and 2 presented evidence of first flush ($b < 1$) for almost all sizes of MPs except for those larger than 2,000 μm (Figure 4-3a and Figure 4-3b). Over 50% of these MPs were typically discharged within the initial 22–32% and 36–40% of the flow volumes in Events 1 and 2, respectively. At the same time, relatively more substantial first flush effects were noted for MPs smaller than 40 μm during these light to moderate rainfall events ($b = 0.5–0.72$; 40–45% mass discharge during the initial 20% of the flow). In Event 3, MPs sized 100–300 μm clearly showed the first-flush behavior (Figure 4-3c). However, the characteristic curves of other size clusters appear below the identity line, indicating a final-flush behavior (Qin et al., 2016), where 50% of the mass discharges occurred in the latter half of the flow. Regardless of the rainfall event, MPs larger than 2,000 μm showcased the final flush phenomenon, in which flow volumes over 45% were required for the transmission of a significant proportion of particles.

These results suggested the early discharge of MPs smaller than 40 µm compared to the larger ones, particularly during light to moderate rainfall events (during Events 2 and 3). In other words, small-sized MPs are easily mobilized with smaller flow volumes induced at light rainfall intensities; whereas large MPs require more energy (i.e., momentum) in terms of flow volumes produced by higher rainfall intensities. While there is scarce evidence on the temporal emission patterns of microplastics in runoff based on particle size, plenty of similar studies on suspended solids and other inorganic pollutants also showed that the finest particles are eroded first, at the initial stage of a rainfall event, and therefore, are more likely to exhibit first flush effects than larger particles (Zafra et al., 2008). Apart from that, a few recent studies on microplastics in surface runoff emphasized the occurrence of first flush, without considering size-specific emissions characteristics (Cho et al., 2023; Sun et al., 2023). Understanding the detailed characteristics of the first flush at the catchment scale is beneficial in developing mitigatory measures for microplastic pollution of urban rivers.

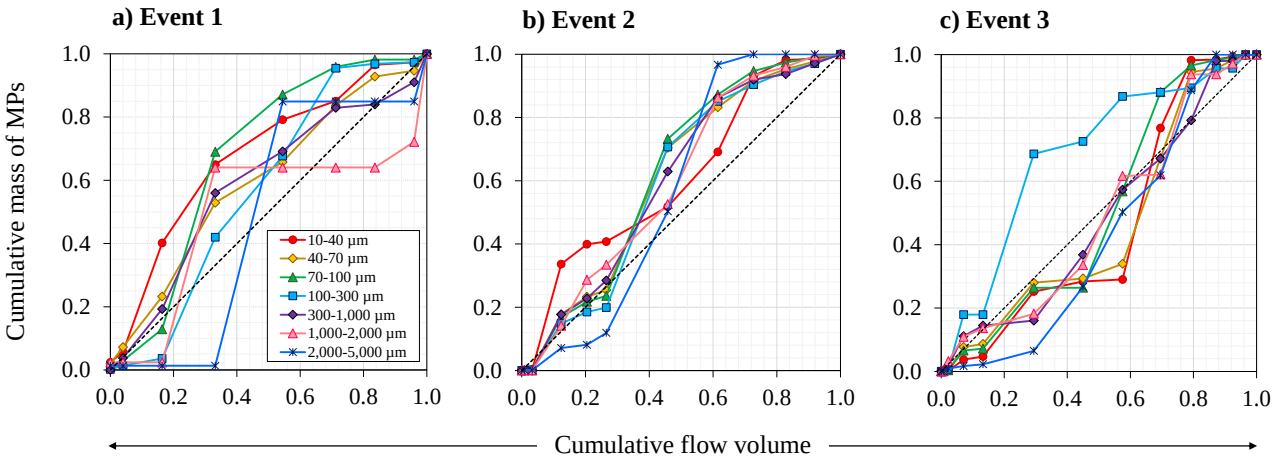


Figure 4-3 *M(V)* curves for microplastic emissions in river during rain
(These curves indicate cumulative mass emissions of microplastic particles (MPs) of different size classes with respect to river flow volume during a) Event 1, b) Event 2, and c) Event 3; the identity line is represented by the black dotted-line with slope = 1.)

The results further suggested that heavy rainfall events are effective in mobilizing larger MPs significantly, compared to moderate rainfall events (24 mm). The preceding rainfall episode before Event 3 (34 mm rainfall before 2 days) might have already washed off a considerable proportion of small MPs from the land, as portrayed by the low quantities of MPs observed in the early stage of Event 3. Nonetheless, it was not strong

enough to mobilize MPs larger than 2,000 μm, which were likely remained on the land until mobilized during the current event. Moreover, the strong rainfall intensities might have scoured the sediments in stormwater canals as well, giving rise to the higher loads of large MPs that were previously deposited (Sang et al., 2021). In addition to that, these intensive rainfall conditions (Event 3) triggered a final flush of MPs smaller than 70 μm, ascribing to the post-rainfall, turbulent flow conditions. Microplastics smaller than 100 μm are believed to be deposited in riverbeds during dry periods, due to "hyporheic exchange", a process that facilitates the movement of solutes between the water column and adjacent groundwater systems (Drummond et al., 2022). This would explain the surge in the small MPs, during the extensive flow mixing following a storm event. Hurley et al. (2018) observed a similar occurrence in the rivers of northwest England, following a flood event.

4.3.3 Runoff-induced changes in the quantities and characteristics of microplastic particles compared to dry weather

The factors by which the concentrations and loads of MPs in each size class increased during the three events, compared to the dry weather, are shown in Figure 4-4a. Overall, the most momentous impact was noted on 300–1,000 μm MPs regardless of the magnitude of the rainfall (EMCs increased by 140, 760 and 840 times; and loads increased by 260, 2,140, 3,730 times for Events 1, 2 and 3, respectively). This can be partly attributed to the relatively lower presence of 300–1,000 μm MPs in the dry-day samples (Figure B–3), possibly caused by gravitational settling (F. Xia et al., 2023). However, increased fractions of 300–1,000 μm microplastics compared to smaller or larger particles have also been noted in Qin River, China, following a rainfall event (Wei et al., 2022). Besides, the size distribution of microplastics in road dust from Japan and overseas also comprised relatively higher contents of microplastics in this size range (Morioka et al., 2023; Yukioka et al., 2020), reflecting the transformations in the size composition of riverine microplastics caused by runoff.

The results further depicted that moderate rainfall events with long ADDs (Event 2) may exert a higher impact on 40–300 μm MPs, possibly due to the increased accumulation during long ADDs. In particular, MPs sized 100–300 μm were heavily increased by such events (EMC increased by 580 times; load increased by 4,200 times), depicting the highest mass inputs recorded for any size class of MPs. The mass percentages

of microplastics, as well as the traffic-related road dust, were maximized around the size range of 125–300 µm, complementing the present observations (Morioka et al., 2023; Shen et al., 2016). The studies on road dust suggested higher accumulation densities for smaller particles compared to larger ones with increased ADDs (Yuan et al., 2017). On the other hand, heavy rainfall events characterized by short ADDs (Event 3) may significantly affect MPs larger than 300 µm, due to the increased force exerted by strong runoff flows; and 10–40 µm smallest MPs, due to the scouring of riverbeds (explained in Section 4.3.2).

Overall, Events 1, 2, and 3 resulted in 4-, 110-, and 40-fold increased EMCs and 10-, 350- and 320-fold increased loads compared to the dry weather. By means of a conservative estimation, we speculated that even though wet days constitute only 30% of a typical year in Japan, this period collectively contributes to 98% of the annual mass emissions of MPs (96% in terms of number) along the river compared to the dry days (Table B–2). The number of days with light rainfall events is high compared to moderate and heavy rainfall days but indicated the least contribution to annual loads (1%); hence, the target rainfalls for river microplastic emission control should be moderate to heavy rainfall episodes, especially when associated with longer ADD periods. In fact, these findings established that wet periods may impose more severe impacts on riverine microplastic emissions than previously evaluated (Eo et al., 2019).

The polymer composition of MPs was also affected distinctively by the runoff inflows (Figure 4-4b). As evident from many previous studies, polyethylene (PE) constitutes the dominant polymer type in river water, owing to its extensive applications across the globe (Plastic Europe, 2022). While this complimented the present findings, a considerable reduction in the PE content was noted during rain due to the increased fractions of other polymer types. The proportions of PP (polypropylene) were less compared to PE and significantly increased during Event 2 (25% in terms of mass), possibly due to the continuous fragmentation and accumulation on the land surface during the dry days. Some studies performed comparative investigations of polymer distribution before and after rainfall, which did not capture the transitional effects caused by rain (Gündoğdu et al., 2018; Wei et al., 2022).

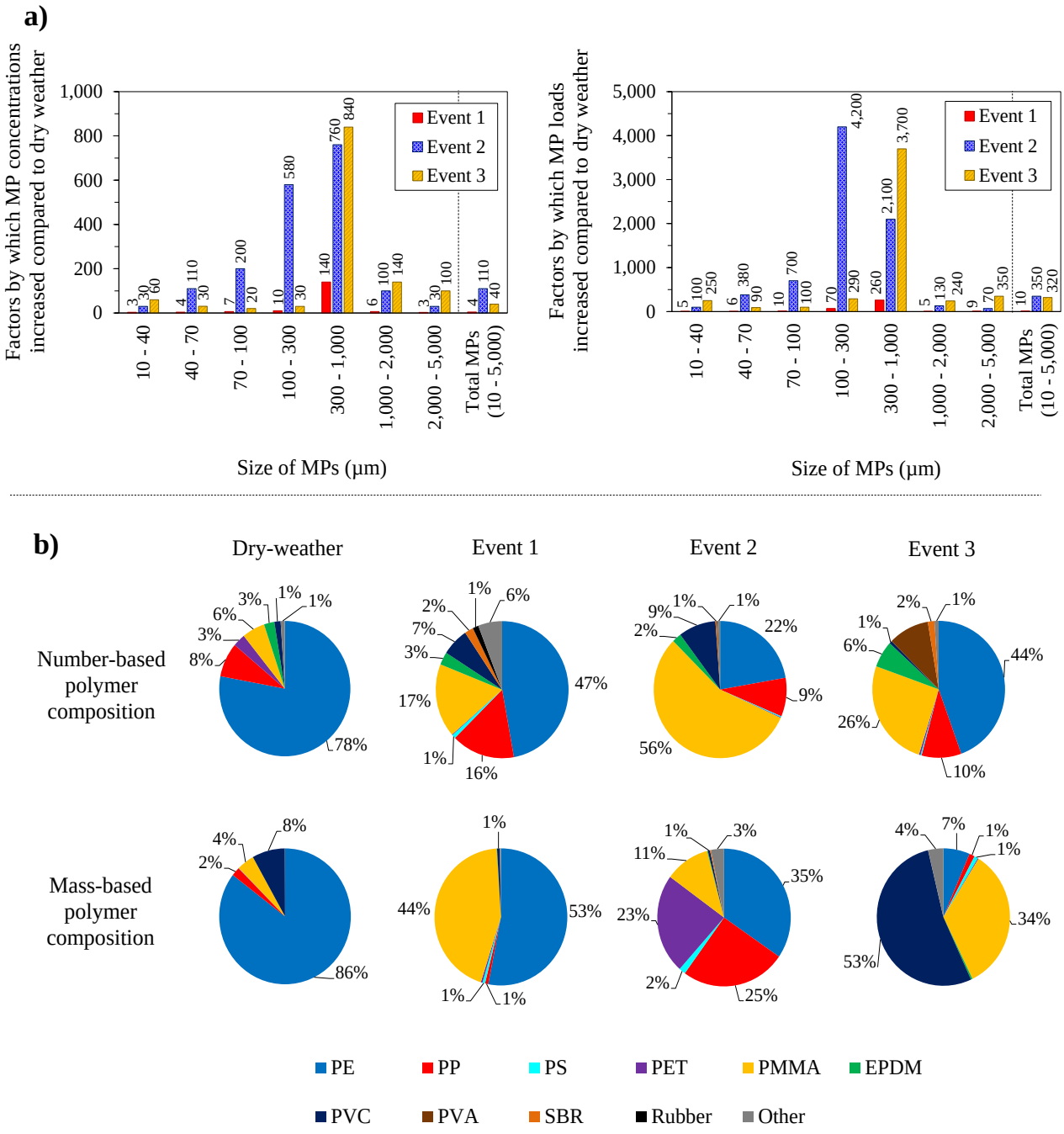


Figure 4-4 Surface-runoff driven changes to the distribution of microplastics in river a) the factors by which the concentrations and loads of microplastic particles (MPs) increased due to the three rainfall events, compared to dry weather; and b) the polymer composition of MPs during the three rainfall events compared to dry weather (PE – polyethylene; PP – polypropylene; PS – polystyrene, PET – polyethylene terephthalate; PMMA – polymethyl methacrylate; EPDM – ethylene propylene diene monomer; PVC – polyvinyl chloride; PVA – polyvinyl alcohol; and SBR – styrene-butadiene rubber).

The runoff introduced extraordinarily high amounts of polymethyl methacrylate (PMMA) into the river, both by number (17–56%) and mass (11–44%), during all three events. Microplastics in road dust samples collected from various parts of Japan, including the study region, comprised considerable proportions of acrylic resins, including PMMA, potentially derived from road marking paints (Kitahara & Nakata, 2020; Yukioka et al., 2020). Additionally, polyvinyl chloride (PVC), polyvinyl alcohol (PVA), and polyethylene terephthalate (PET) were detected at considerable amounts and masses during moderate to heavy rain, inferring enhanced mobility of denser MPs (1.38–1.40 g/cm^3) due to increased rainfall. PVC particles, likely originating from road markings and plumbing work, were also frequently detected in road dust samples from Japan (Kitahara & Nakata, 2020; Morioka et al., 2023). Such dense polymers have been recovered from the sediments of stormwater pipes due to high settling rates (Sang et al., 2021). Small quantities of traffic-related MPs, such as styrene-butadiene rubber (SBR) and synthetic rubber, were also detected during the rainfall events, but not on dry days. Additionally, the fractions of ethylene propylene diene monomer (EPDM), were fairly increased during rain.

4.3.4 Variability of microplastic fibers during rain events

The temporal variations and the inter-event variations in the abundances of MPFs were comparable to those of MPs (Figure 4-5a and Figure 4-5b), implying a similar influence on both MP particles and fibers by rainfall characteristics. To elaborate, MPFs peaked at the highest intensity in Events 1 and 2 and during the post-rainfall turbulence in Event 3. The EMCs were 6,780 items/m^3, 28,440 items/m^3, and 15,060 items/m^3; and the loads were 210 g, 1,890 g, and 3,950 g, respectively, for Events 1, 2, and 3. Interestingly, the size-specific inter-event variations in MPFs (Figure 4-5c) also demonstrated a significant increase in 100–300 µm MPFs in Event 2 (EMC increased by 20-folds; load increased by 36 folds), similar to MP particles. This further emphasizes that MP particles and fibers of 100–300 µm are more prone to accumulate on land surfaces during long dry periods and mobilize via runoff compared to other sizes of microplastics. In addition, MPFs smaller than 100 µm were strongly impacted by heavy rainfall events (Event 3). These small MPFs (<500 µm) are heavily retained by the river sediments (Ding et al., 2019; Yin et al., 2022), potentially attributed to the active “turbidity currents” (Pohl et al., 2020). These buried MPFs are supposedly resuspended into the water phase during vigorous flow mixing following a storm.

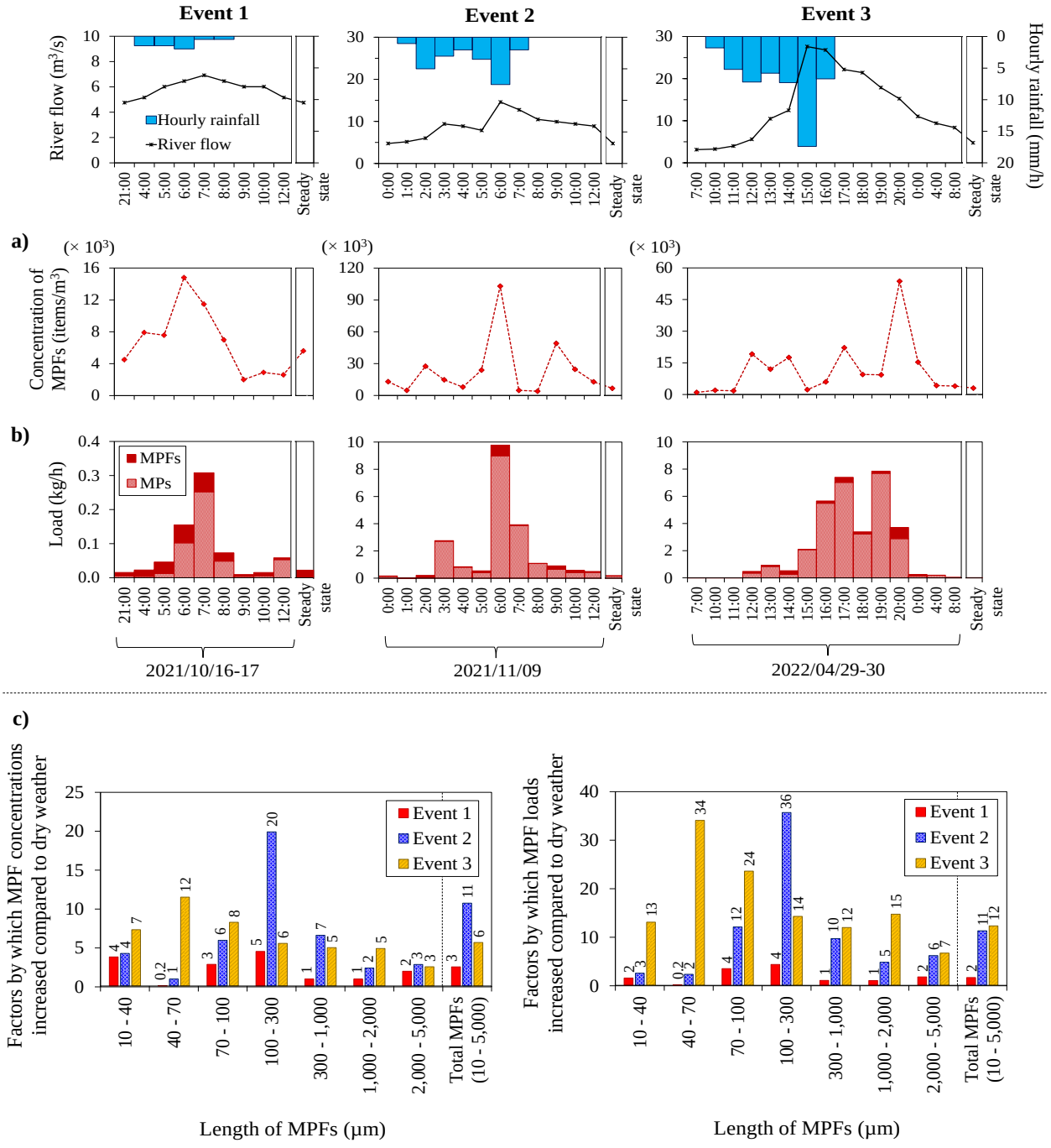


Figure 4-5 Temporal variations of MPF concentrations and loads in river water during rain and their increment compared to dry weather

a) variations of the number concentrations of MPFs and b) variations of the mass emissions of MPFs compared to MPs during the three rainfall events; c) the factors by which the concentrations and loads of MPFs increased due to rainfall events, compared to dry weather ("MPs" refers to microplastic particles, and "MPFs" refers to microplastic fibers).

Irrespective of the said similarities in the trends of the dynamics in MPFs, the proportions of MP particles were generally high compared to MPFs over the course of all three rainfall events (Average proportions of MPs out of the total MPs and MPFs: Event 1 – 54%, Event 2 – 75%, and Even 3 – 68%) (Figure 4-5b). Moreover, the increased concentrations and loads of MPFs during the rainfall events compared to the dry days were not as high as the incremental factors for MP particles (Figure 4-5c). During dry days, the loads of MPFs (mass-based) were three times larger than the particles (Table B2). In contrast, the relative proportions of MP particles (compared to MPFs) increased during rain, resulting in two times higher loads than MPFs in Event 1, and 10 times higher loads in Events 2 and 3, respectively. Moreover, the contribution of wet periods to the annual loads of MPFs conveyed through the river was also low (67% for mass loads, 76% for number loads) compared to the contribution to MP particles (Table B–2). This denoted a lower impact on the quantities of fibers compared to particles by rainfall-induced runoff.

MPFs are primarily derived from wastewater discharges and atmospheric fallouts (Carr, 2017; Dris et al., 2016). In wet weather, combined sewer overflows (CSOs) are recognized as a crucial source of MPFs due to the interception of sewage discharges with rainwater inflows (Dris et al., 2018; Sun et al., 2023). The urban catchment under investigation is located within a developed region in Japan where wastewater is systematically disposed via separate sewers; therefore, MPFs derived from sewer discharges may not be impacted by rain in the present scenario. In agreement, Treilles et al. (2021) ascertained no relationship between stormwater flows and microplastic fiber concentrations in the rivers of Greater Paris, where separate sewers were employed. In addition to CSOs, atmospheric fallouts are recognized as indispensable sources of MPFs during rain (Dris et al., 2016); thus, the increased loads in the present study can be assumed to have derived from both real-time atmospheric fallouts and previous depositions on the land.

4.3.5 Relationships with total suspended particles, and implications for pollution control

The number and mass concentrations of MPs indicated positive correlations with the dynamics of total suspended solids (TSS) during the three events (Figure B–4 and Figure 4-6), demonstrating a close association of MPs with the accumulated particles on land, e.g., in road dust. As shown in Figure 4-6, the concentrations (mass) of MPs between

40–100 µm were well-correlated with TSS (R^2 = 0.52–0.95), regardless of the intensity of rainfall. Additionally, MPs ranging between 100–1,000 µm showed significant associations with TSS during light to moderate rainfall events, with 100–300 µm MPs depicting the strongest correlations (R^2 = 0.63–0.96), confirming a significant contribution to this size cluster by the runoff. Moreover, moderate rainfall events characterized by higher ADDs reflected the strongest correlations out of the three rainfall scenarios, depicting similar build-up and wash-off processes for both TSS and MPs of a wide size range.

The heavy rainfall episodes portrayed rather poor correlations for most of the size clusters, confirming the effect of turbulent flow conditions discussed above. However, the emissions of larger MPs (1,000–5,000 µm) during such events can be substantially attributed to the accumulated road dust (R^2 = 0.55–0.65) than to the flow dynamics. On the contrary, the weak correlations derived for 10–40 µm implied a unique dynamic trend (e.g., complex atmospheric aerosolization, suspension, and deposition) for tiny MPs that is distinctively different from the behavior of the typical non-point source pollutants.

Kataoka et al. (2019) revealed no links between TSS and MPs larger than 300 µm in the surface waters of 29 Japanese rivers in the absence of rain. Nonetheless, our study elucidated that such links would be perceptible during rain, due to the external inputs of MPs via runoff. It also implied that the dynamics of MPs may mimic the non-point source pollutants that are simultaneously discharged along with the runoff flows. Since continuous monitoring of MPs during a rainfall event can be strenuous, alternative measurements (e.g., TSS) could be useful in predicting the dynamics of MPs. Moreover, the control mechanisms for such pollutants could be explored for size-targeted mitigation of MPs conveyed through runoff as well.

The global reports presented numerous approaches of stormwater management (Wang et al., 2022), in which the efficiencies are highly sensitive to particle size and have been shown to perform poorly in removing microplastics smaller than 100 µm (Smyth et al., 2021; Ziajahromi et al., 2020). This means that, the conventional stormwater management measures would be more convenient for controlling 100–300 µm and 300–1,000 µm MPs, which are heavily affected by rain, and can be easily predicted with the dynamics of TSS, but not for the smaller debris. Nevertheless, the effective control of the emissions of such small particles is crucial concerning their extremely high abundance, ability to interfere with biological life and the abstruse nature of the emission dynamics.

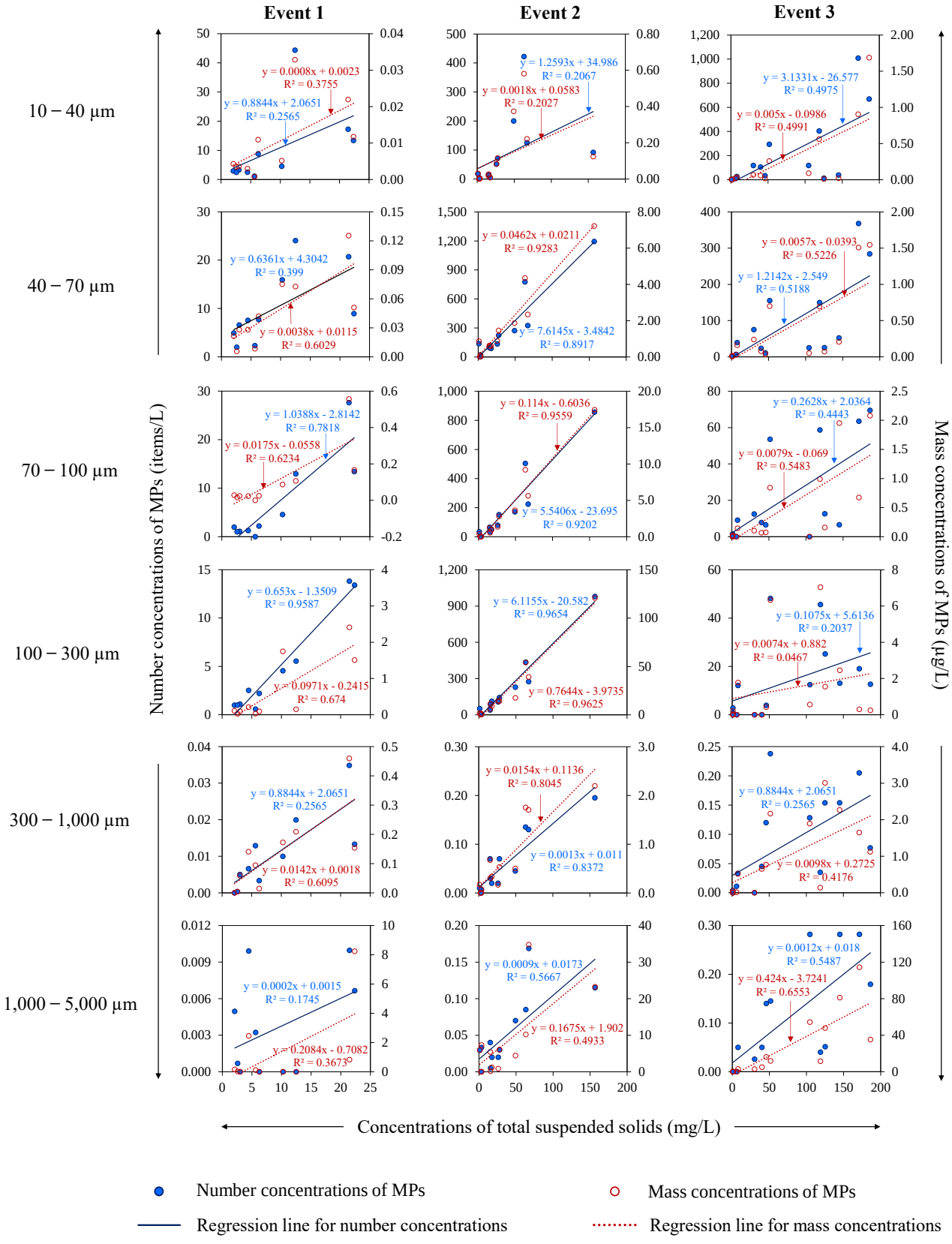


Figure 4-6 Correlations between the concentrations of total suspended solids (TSS) and microplastic particles (MPs) of different size clusters
(All the left y-axes represent the number concentrations of MPs in items/L, while the right y-axes denote the mass concentrations of MPs in µg/L).

As shown in this study, an approach like *M(V)* curves (described in Section 4.3.2) can be assisted in planning the optimum interventions for size-targeted emission control of microplastics at the catchment scale, in conjunction with the continuous and frequent monitoring of microplastic build-up and wash-off processes under different rainfall scenarios.

4.4 Conclusions

To the best of our knowledge, this study demonstrated the first insights on the inter-event and intra-event dynamics of the microplastic particles (MPs) and fibers (MPFs) in an urban river by sampling at a high frequency over the course of three different rainfall events (light, moderate, and heavy). We showed that numerous rainfall characteristics may act synergistically to influence the size-specific emission patterns for MPs and MPFs. In general, MPs as small as 10–40 µm are shown to be rapidly mobilized at lower rainfall intensities, indicating first flush effects, whereas those larger than 2,000 µm are discharged at higher rainfall intensities. Subsequently, we suggested that intercepting (and treating) the initial 40% of the runoff that is directly discharged into the rivers may avert microplastic pollution to a significant extent. We further revealed the momentous impacts of rainfall events on 100–300 µm and 300–1,000 µm size clusters of MPs in the river water, and the opportunity to predict their dynamics using typical non-point source pollutants like TSS, when planning interventions for microplastic pollution. In addition, we discovered that MPFs in rivers are trivially impacted by the runoff inflows compared to MPs. Ultimately, this study provided a perfect outset for alleviating rainfall-induced pollution of urban rivers through frequent and continuous monitoring of microplastic discharges at the catchment scale, considering the regional rainfall patterns

CHAPTER 5. A mass balance approach to quantify annual microplastic emissions of urban catchments: surface runoff *vs* wastewater sources

5.1 Introduction

Plastic pollution, including the ubiquitous environmental distribution of microplastics (<5 mm in size), remains an emerging threat to the sustenance of ecosystems and biological lives (Andrady, 2015). Microplastic research spanning over a decade has revealed plenty of knowledge on the abundance, characteristics, occurrence, and distribution patterns of microplastics in urban clusters by investigating water, sediment, and biota in terrestrial and freshwater systems, wastewater discharges, surface runoff, and atmospheric fallouts (Baldwin et al., 2016; Eo et al., 2019; Leslie et al., 2017; Mason et al., 2016; Murphy et al., 2016; Piñon-Colin et al., 2020). The spatial distribution of microplastics is found to be linked with various land use patterns (F. Liu et al., 2019; Yonkos et al., 2014). For instance, data have shown that the global occurrence of microplastics is prominent across urban catchments that represent the hotspots of anthropogenic activities (Kataoka et al., 2019; Yonkos et al., 2014). Moreover, the temporal variations (and seasonal trends) indicate significant fluxes of microplastics in freshwater during wet periods (Eo et al., 2019; Hitchcock, 2020).

Past studies have estimated the annual stocks of plastic debris including macroplastics and large plastic litter (Castro-Jiménez et al., 2019; Gasperi et al., 2014; Jambeck et al., 2015; Kawecki & Nowack, 2019; Lebreton et al., 2017; Lechner et al., 2014; Mai et al., 2020; Meijer et al., 2021; Schmidt et al., 2017; Van Der Wal et al., 2015; Van Emmerik et al., 2019), and microplastics (Clayer et al., 2021; Eo et al., 2019; Fan et al., 2019; Kawecki & Nowack, 2019; Mai et al., 2019; Sullivan et al., 2023; Treilles et al., 2022; Wagner et al., 2019; Whitehead et al., 2021; F. Xia et al., 2023), that are conveyed from land to freshwaters, and oceans through the river systems. Table 5-1 provides the meta-synthesis of previous studies that specifically quantified the annual emissions of microplastics into the receiving waters through numerous sources (Abusafia et al., 2023; Baensch-Baltruschat et al., 2021; Boucher et al., 2019; Chen et al., 2020, 2022; Cheung & Fok, 2017; Cho et al., 2023; Conley et al., 2019; Dris et al., 2016, 2018; Evangeliou et al., 2022; Jan Kole et al., 2017; Järlskog et al., 2020; Magnusson et al.,

2016; Nizzetto, Bussi, et al., 2016; Ono et al., 2023; Piehl et al., 2021; Rebecca Sutton et al., 2019; Schmidt et al., 2020; Siegfried et al., 2017; Unice et al., 2019; van Wijnen et al., 2019; L. Zhang, Xie, et al., 2020; Y. Q. Zhang et al., 2021; Y. Zhou et al., 2023), including both model-based research and field studies performed at the regional and global scales.

The lumped catchment-based emissions of microplastics range from 0.03 to 1.40×10^7 tons per annum with limited information on various source contributions (Table 5-1). Accordingly, there remains scarce evidence on the mass-based source composition of the annual discharges. Furthermore, there is a limited understanding of the composition of annual emissions from the point of view of managed/controlled and unmanaged/uncontrolled sources, which is imperative for planning interventions for microplastic pollution. While controlled sources are primarily represented by WWTP effluents (point sources) (Carr, 2017; Murphy et al., 2016), uncontrolled sources are mainly denoted by untreated surface runoff and atmospheric depositions (non-point sources) (Cho et al., 2023; Dris et al., 2016; Piñon-Colin et al., 2020). Although these sources have already been explored as vital sources of microplastics, their comparative contribution to the microplastic pollution of the urban catchments and the receiving rivers, which act as the primary conduits of the land-sourced microplastics into the global oceans is poorly understood (Meijer et al., 2021). Moreover, these comparative emissions have also not been analyzed in terms of different size-clusters of microplastic particles, even though their mobility would be differently affected during the highly dynamic runoff processes (Cho et al., 2023).

Considering the aforementioned gaps in the existing research, the present study aims to explore a conservative-rational approach to quantify the annual microplastic stocks of an urban catchment and its impact on the receiving river network in metropolitan Kyoto City, Japan. In this watershed, systematic waste management facilitates the conveyance of all blackwater, and greywater generated within the catchment into WWTPs via a separate sewerage network, and the direct discharge of rainwater and runoff into the river network through stormwater canals. This enabled the classification of all sorts of microplastic discharges within the catchment into two broad categories, as “controlled emissions” (hereinafter referred to as “CE”), which represent the discharges that are appropriately conveyed through sewer networks and managed at WWTPs, and “uncontrolled emissions” (hereinafter referred to as “UCE”), which denote the direct

releases of microplastics into the river network without any management.

The key objectives of this study include

1. comparing the magnitude and characteristics of microplastics in the sources contributing to CE and UCE;
2. quantifying the annual microplastic emissions from an urban catchment and resolving the relative contribution of uncontrolled discharges, e.g., surface runoff and regulated wastewater emissions; this will further enable an absolute clarification of the role of WWTPs in controlling microplastic releases to the receiving waters on seasonal and annual bases; and finally,
3. providing insights on the surface area-normalized microplastic pollution in urban catchments, in comparison to previous reports from several urban catchments worldwide.

We discuss the attributes in terms of multiple-size clusters of microplastics within the total size range of 10–5,000 µm and highlight the importance of employing mitigation strategies to manage microplastic emission in surface runoff. The findings of this study will provide valuable insights to derive effective management strategies for microplastic pollution abatement of urban agglomerations and the adjoining receptor water environments in both developed and developing regions globally. Appendix C provides the supplementary information relevant to this study which shall be referred to in conjunction with Chapter 5.

Table 5-1 Summary of literature reporting annual microplastic emissions from various sources into the receiving waters

Reference	Study area / Catchment	Catchment area (km^2)	Annual MP emissions	Source contribution to/composition of annual MP emissions	Target particle size/type [b]
Lechner et al., 2014	River Danube, Austria	800,000	1,533 tons/year	Catchment drainage to the Black Sea	mesoplastics: 2,000–20,000 µm MPs: <2,000 µm
Fan et al., 2019	Pearl River Estuary, China	450,000	15,963 tons/year	Catchment drainage to the estuary through the mainstream and tributaries	100–1,000 µm
Wagner et al., 2019	Parthe River, Germany	Urban: 245 Rural: 150	3×10^6 items/year 2.6×10^4 items/km^2/year	Catchment drainage to the river (90% of the emissions are conveyed during 20% of the year)	macroplastics and MPs: >500 µm
Sullivan et al., 2023	River Tamar Estuary, UK	1,800	0.027–0.043 tons/year	Catchment drainage to the estuary	200–2,500 µm
Unice et al., 2019	Seine River, France [a]	78,000	1.8 kg/inhabitant/year 500 inhabitants/km^2	Catchment drainage (18% is released to freshwater and 2% reaches the estuary)	TRWP: 0.5–200 µm
Clayer et al., 2021	Lake Mjøsa, Norway [a]	17,028	7.4−119.4 tons/year (average: 35.9 tons/year)	Catchment drainage (70−90% is transferred to the ocean)	75−5,000 µm
Whitehead et al., 2021	River Thames, UK [a]	10,000	100 tons/year	Catchment drainage	1−1,000 µm
Treilles et al., 2022	Sein River, France	889	924–1,675 tons/year	Catchment drainage to the river; a major flood event that spanned 14.5% of the year contributed 40% of the annual loads	MPs: 32−2,528 µm MPFs: 313−32,328 µm
Eo et al., 2019	Nakdong River, South Korea	21,588	5.4–11.0 trillion items/year 53.3–118.0 tons/year	Catchment drainage (81 % of the loads are transported in the wet season)	20–5,000 µm
Schmidt et al., 2020	Ten major river basins in Germany	409,591	7×10^{12} items/year	WWTP emissions of the river basins	10–5,000 µm
Van Wijnen et al., 2019	A global study [a]	-	$(4.7–7.1) \times 10^4$ tons/year	Emissions through sewerage discharges (primarily originating from car tire wear and laundry fibers) contribute to 20% of the global emissions (1% in Africa to 60% in OECD countries)	-
Siegfried et al., 2017	European river basins [a]	-	Total riverine MPs transferred to European Seas: 14.4 kilotons/year (0-192 kg/km^2/river basin/year)	Emissions from point-sources: TRWP (42%), plastic-based textiles abraded during laundry (29%), synthetic polymers and plastic fibers in household dust (19%) and microbeads in personal care products (10%).	10–400 µm
Chen et al., 2020	Shanghai Megacity, China	6,340	8.50×10^{14} items/year	CSOs in wet weather (six times larger than WWTP effluent discharges)	80–5,000 µm
Y. Zhou et al., 2023	Nanning, South China	15	5.83×10^{10} items/km^2/year	Catchment drainage including CSOs (60% emissions occur in wet weather)	30–5,000 µm
Piehl et al., 2021	Warnow River, Germany	3,280	152–291 billion items/year	Emission to the Baltic Sea: Catchment emissions (49.4%), separated city stormwater system (43.1%), CSO discharges (6.1%), and WWTP effluent (1.4%).	10–1,000 µm
Rebecca Sutton et al., 2019	San Francisco Bay tributaries, USA [a]	6,725	7 trillion items/year	Emissions to the bay through tributaries (stormwater loadings of MPs are 300 times higher than WWTP loadings)	>125 µm
Cheung & Fok, 2017	Aquatic environments in mainland China	-	306.9 tones/year 209.7 trillion item/year	Emissions to aquatic environments from mainland China (80% of the emissions originate from WWTP effluents)	microbeads: 24–800 µm
Conley et al., 2019	Charleston Harbor, South Carolina, USA [a]	-	0.1–0.2 tons/year 0.34–0.68 g/capita/year	WWTP effluents (accounts for <0.1% of the total plastic emissions to surface waters)	>60 µm
Abusafia et al., 2023	An urban catchment in Kaiserslautern, Germany	3,500	189 kg/year	Catchment drainage (wet-weather emissions to the receiving waters are 2–4 times higher than dry-weather emissions)	5–1,000 µm

Table 5-1 Summary of literature reporting annual microplastic emissions from various sources into the receiving waters (continued)

Reference	Study area / Catchment	Catchment area (km^2)	Annual MP emissions	Source contribution to/composition of annual MP emissions	Target particle size/type [b]
Y. Q. Zhang et al., 2021	A global study (based on literature)	-	2.53–59.00 kg/year	Global emissions from synthetic textile washing via WWTP discharges	MPFs: 0.1 µm–15 mm
Chen et al., 2022	Huangpu River, China	6,340	5,317.7 ± 2,175.3 tons/year (dry) 3,320.1 ± 953.6 tons/year (wet)	Composition of total emissions to receiving waters (3,207.4 ± 1071.6 tons/a): wet weather overflow (23.7%), direct atmospheric fallout (21.7%), WWTP effluent (14.2%), industrial wastewater (14.1%), and surface runoff (10.4%).	80–5,000 µm
Boucher et al., 2019	Lake Geneva basin, Switzerland / France [a]	7,999	55 tons/year	Composition of total emissions to Lake Geneva: river discharge in wet period (71%); urban runoff (15%); River discharge in dry period (9.6%); storm overflow (4.4%); WWTP effluent & atmospheric fallouts (insignificant)	300–5,000 µm
Baensch-Baltruschat et al., 2021	Road network in Germany	-	7.52–9.84 × 10^4 tons/year	TRWP emissions from German road network (12–20% of the total emissions are diverted to surface waters i.e., 8700–19,800 tons/year)	TRWP: <5,000 µm
Evangeliou et al., 2022	A global study [a]	-	3.3–14.0 × 10^{12} g/year	Riverine emissions of MPs and MPFs to the global oceans	atmospheric MPs: 250 µm atmospheric MPFs: 2,500 µm
Mai et al., 2019	Eight major river outlets of the Pearl River Delta, South China	-	39 billion items/year (66 tons/year)	Drainage of riverine catchments to the river delta	300–5,000 µm
Kawecki & Nowack, 2019	Switzerland	-	Macroplastics: 13.3 ± 4.9 g/cap/year MPs: 1.8 ± 1.1 g/cap/year	Total emissions to freshwater from various sources	Seven commodity plastics macroplastics (>5,000 µm) MPs (<5,000 µm)
Ono et al., 2023	Tokyo Bay watershed, Japan	-	personal care products: 10.2 ± 1.6 tons/year MPFs: 38 ± 22 tons/year tire-wear particles: 1,500–1,800 tons/year	Total emissions to the bay from various sources	personal care products: 300 µm MPFs: 100 µm (length) × 5 µm (diameter) tire-wear particles: 10–100 µm

[a] Model-based studies
[b] The target particle type is microplastics (MPs) unless stated otherwise

Note: Only the studies that assessed annual microplastic emissions from a particular catchment to the receiving waters, or from freshwaters (e.g., rivers) to the oceans are listed in this table. Those that estimated annual depositions of (micro)plastics on the land/in soil from various sources (e.g., atmospheric fallouts and sewage sludge) and in sediments in aquatic environments; and annual emissions of macroplastic debris or plastic litter are not included here but cited in the Introduction section of the main text.

Abbreviations:
MPs: microplastics
MPFs: microplastic fibers
TWRP: tire and road wear particles
CSO: combined sewer overflow
WWTP: wastewater treatment plant

5.2 Materials and methods

5.2.1 Study area

A sub-catchment of the Katsura River basin, which spans across the metropolitan Kyoto City in Japan, was selected as the study area (catchment area = 280 km^2, Figure 5-1). The river network of the catchment comprises two major rivers, Kamo and Katsura. The two rivers originate in the northern region of Kyoto and flow towards the south to merge and thereafter continue as the Katsura River. In the downstream, it becomes a major tributary to the Yodo River, the primary source of drinking water for the entire population in Osaka prefecture, and finally reaches the sea at Osaka Bay.

When delineating the boundary of the sub-catchment (Figure 5-1), we determined the specific inlet and outlet points based on the serving areas of two principal WWTPs in Central Kyoto (Figure C–1). The WWTPs receive all backwater and greywater generated at households, offices, and industries (pre-treated wastewater) for further treatment (JSWA, 2021). The rainwater collected through gutters and drains and surface runoff are directly conveyed to the river network via separate stormwater canals. The treated effluents produced in the two plants are also discharged into the river network through multiple outlets, as shown in Figure C–1. This catchment is densely polluted at a rate of 1,782 persons/km^2 and widely occupied with built-up areas towards the downstream of the catchment (Figure C–2).

5.2.2 Sampling

Sampling was conducted during 2021–2022, involving both dry and wet days to account for the effects of weather on the annual microplastic emissions. CE and UCE of microplastics were determined by sampling wastewater from WWTPs and the surface water of the rivers, respectively. We sampled wastewater influent and effluent from the two WWTPs, and river water was collected at three stations, involving the Mikage bridge, Nishioh bridge (inlet of the catchment), and Miyamae bridge (outlet of the catchment) (see Figure 5–1). Wastewater sampling was carried out one time as the flows are not affected by weather in separate sewer systems. River water sampling in dry weather was exercised at all three stations mentioned above on two occasions in August 2021 and October 2021 (sampling procedures described in Section 3.2.2 of Chapter 3). On the other

hand, the wet weather sampling was performed only at the Mikage bridge three times during rainfall events with different characteristics (sampling procedures described in Section 4.2.2 of Chapter 4) shown in Table 5-2. The three events were classified as light (<2.5 mm/h), moderate (2.5–7.6 mm/h), and heavy (>7.6 mm/h), depending on the maximum rainfall intensity (expressed in mm/h) of the event (AMS, 2012).

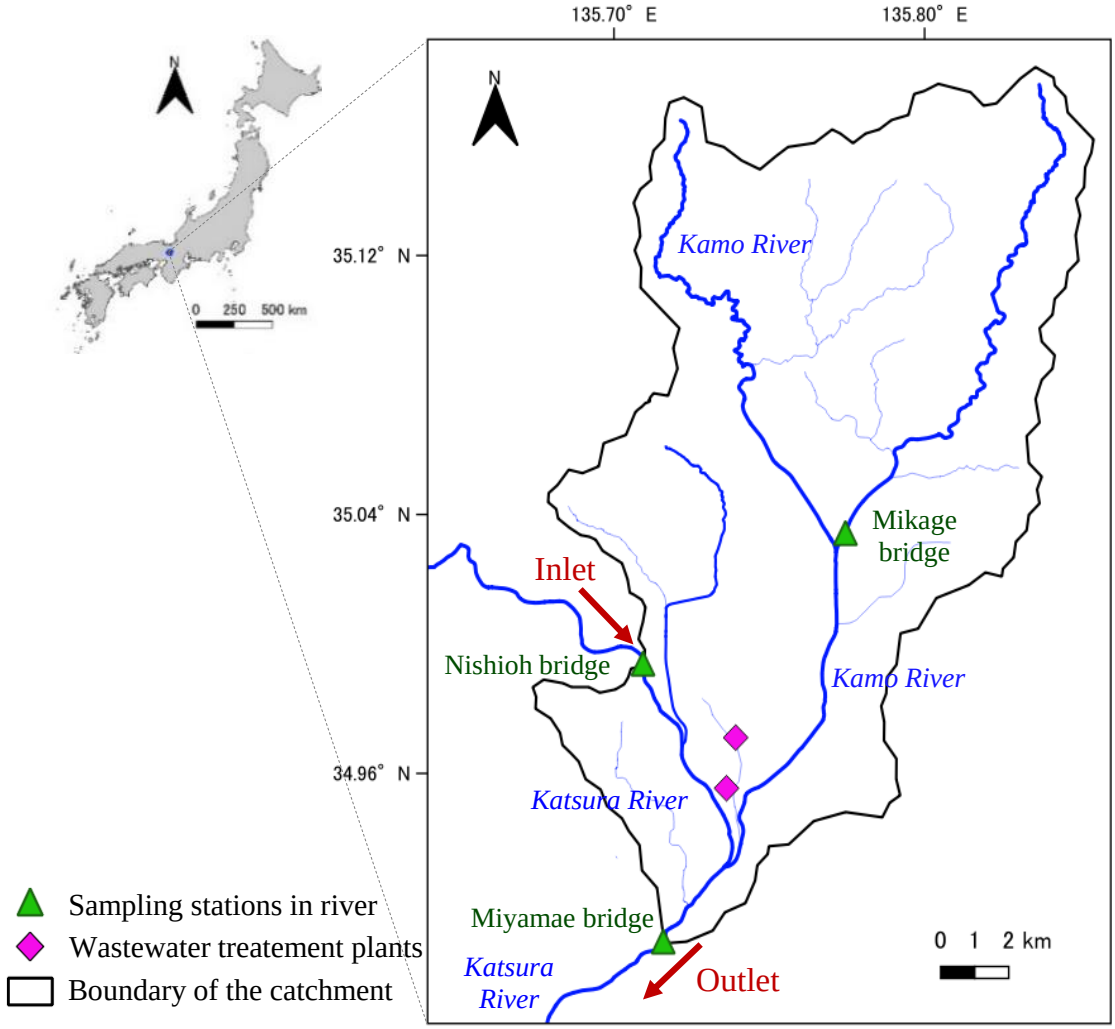


Figure 5-1 The sub-catchment of the Katsura River (study area) and the sampling locations ("Inlet" and "outlet" refer to the points at which the river flow enters and leaves the delineated sub-catchment. Refer to Figures C–1 and C–2 for the effluent outlets of the WWTPs and the land usage map, respectively).

Table 5-2 Characteristics of the three rainfall scenarios (sampling at the Mikage bridge)

	Event 1 (Light rainfall) [a]	**Event 2** (Moderate rainfall) [a]	**Event 3** (Heavy rainfall) [a]
Date and time of the event	2021-10-16 04:00–09:00	2021-11-09 01:00–08:00	2022-04-29 10:00–17:00
Total precipitation (mm)	6	24	52
Duration of rainfall (hours)	5	7	7
Rainfall intensity			
Maximum (mm/h)	2	7.5	17.4
Average (mm/h)	0.3	3.4	7.4
Total river flow (m^3)	193,600	404,900	1,052,500
Number of antecedent dry days	3 days	14 days	2 days
No. of days with similar rainfall events per year [b]	48	35	29

[a] *The definition of rainfall categories (light: <2.5 mm/h; moderate: 2.5–7.6 mm/h; heavy: >7.6 mm/h) was based on the classification of the American Meteorological Society (Rain - Glossary of Meteorology)*

[b] *The number of days per year with light, moderate, and heavy rainfall events were determined based on the daily maximum rainfall intensity. Rainfall data were obtained from the website of the Japan Meteorological Agency for the years 2021 and 2022 (sampling period).*

The sampling involved microplastics spanning in the size range of 10–5,000 µm. River water sampling during dry weather and wet weather followed the procedures described in Section 3.2.2 of Chapter 3 and Section 4.2.2 of Chapter 4, respectively. Wastewater samples were collected at the inlet (for influent samples) and outlet (for effluent samples) of the wastewater treatment plants (WWTPs), separately. Sampling of microplastics in the influent was performed with bulk sampling of wastewater using a stainless-steel bucket. The volume of water filtered for small microplastics (10–300 µm) and large microplastics (>300 µm) were 0.5 L and 100 L, respectively. The influent samples were then filtered through 10 µm and 300 µm mesh-sized plankton nets for small and large microplastics, respectively. Effluent samples were collected by in-situ pump filtration using a submersible water pump operated at a constant speed. The pumped effluent was subsequently filtered through 10 µm and 300 µm mesh-sized plankton nets to obtain small and large microplastic samples, respectively. The volumes of effluent filtered for small and large microplastic samples were 80 L and 7,000 L, respectively. All plankton nets were carefully transferred into re-sealable bags at the end of sampling and transported to the laboratory for further analysis.

5.2.3 Extraction and characterization of microplastics

Microplastics in river water and wastewater were extracted using similar methods with slight differences (e.g., the volumes of chemical solutions used in the pretreatment process) depending on the quantity and quality of background constituents present in the two types of samples. Moreover, the methods of extraction for river water and wastewater followed the procedures of previous studies (Rodrigues et al., 2018; Ziajahromi, Neale, et al., 2017).

The pretreatment process involved wet peroxidation for the digestion of organic matter, followed by density separation for removing inorganic constituents, including sediments (Rodrigues et al., 2018; Ziajahromi, Neale, et al., 2017). Wet peroxidation involved digestion of the samples using 30% H_2O_2 and 0.05 M $FeSO_4$, followed by oven drying at 55 °C, whereas density separation entailed recovering microplastics from the surface of 5.3 M NaI (1.53 g/cm^3) solution. The samples for small microplastics (10–300 µm) and large microplastics (>300 µm) were retrieved separately by vacuum filtration through 0.45 µm polycarbonate membrane filter and 10 µm nylon nets, respectively.

The morphology of large microplastics was observed with a stereoscopic microscope (SMZ-161 Series, Shimadzu, Japan), while the polymer types were detected with Fourier Transform Infrared Spectrometer (Cary 600 Series FTIR, Agilent Technologies, USA) equipped with attenuated total reflectance (ATR). The physical and chemical characteristics of small microplastics were examined with Cary 600 Series µ-FTIR (Agilent Technologies, USA) in transmission mode. Detailed information regarding the extraction procedure, analytical techniques, and quality control measures are presented in Sections 3.2.3 and 3.2.4 of Chapter 3, and Section 4.2.3 of Chapter 4. The concentrations of the environmental samples were adjusted for background contamination using the data from the blank tests which are presented in Table C–1. The results of recovery tests are shown in Table A–7 (Appendix A)

5.2.4 Computational (mass-balance) approach

The concentrations of microplastics were expressed as the number of items (or mass) per unit volume of water. The mass of microplastics was estimated from the number by multiplying the particle volume and the respective polymer density. Depending on the morphology of the particles, their volumes were calculated with Equation 5-1 (Cózar et

al., 2014). It should be noted that this analysis did not involve microplastic fibers.

$$\text{Volume of MPs (fragment, films, and spheres)} = 4/3\pi r^3\alpha \quad (5\text{-}1)$$

Where "*r*" is half of the average of maximum and minimum lengths of MPs; and "α" is the shape factor (0.1 for fragments and films, and 1 for spheres).

This method of calculating mass of microplastic particles is validated in Text A1 (in Supplementary Information for Chapter 3). The calculated masses for microplastics in the size range of 300 µm – 5 mm, which occupies over 94% of the total mass of particles in the size range of 10–5,000 µm would be approximately 4 times (range: 4.3 ± 4.5 times) higher than the measured/actual masses.

The loads of microplastics (in terms of mass) were calculated by multiplying the concentrations and the respective flow rates (river or wastewater discharges expressed in flow volume per unit time). The mass balance approach (Figure 5-2) involved the following steps:

Step 1: Calculate the microplastic concentrations in river water (at all three stations) during dry days and WWTP influent and effluent (Table 5-3).

Step 2: Calculate microplastic concentrations and loads in the river (Mikage bridge station) under the three rainfall scenarios (Refer to Chapter 4).

Step 3: Estimate the factors by which the microplastic concentrations and loads increased during the three rainfall scenarios compared to a dry day (Figure 4-4a of Chapter 4). Considering the flow continuity in a river, these factors were used to estimate microplastic concentrations and loads at the catchment inlet and outlet for the same rainfall scenarios.

Step 4: Estimate the annual microplastic budget of the watershed as follows.

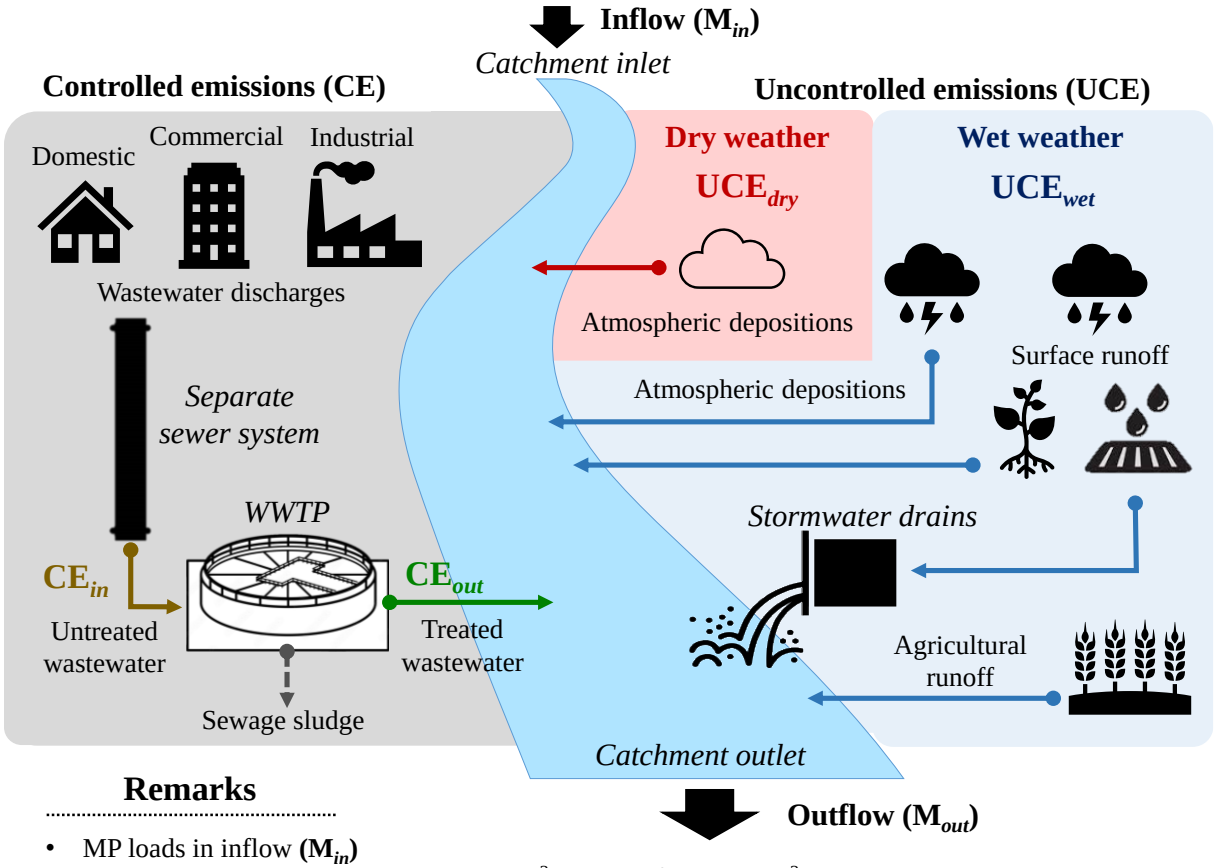
Figure 5-2 depicts the sources and transmission pathways of CE and UCE of microplastics. The term CE represents the wastewater discharges that are adequately conveyed to the WWTPs through separate sewer systems; the untreated component represents the total microplastics from domestic and industrial wastewater and is defined as CE_{in}, while the treated component, i.e., WWTP effluent, discharged to the river network is defined as CE_{out}. UCE in wet weather (UCE_{wet}) primarily denotes the combination of the microplastic transmissions due to runoff inflows and direct atmospheric fallouts, while UCE in dry weather (UCE_{dry}) indicates the background

emissions of microplastics due to atmospheric depositions.

Figure 5-2 assembles the formalisms for expressing the annual microplastic emissions of the catchment. While the estimated annual emissions are based on average microplastic concentrations derived for the sources of CE and UCE, a range of possible values are determined in Text C–1. The assumptions involved in the analysis are as follows.

- UCE of microplastics are not impacted by the hydrodynamics of the river and stormwater pathways. Meaning that, the deposition of microplastics due to gravitational settling and resuspension of microplastics deposited in sediments due to turbulence are considered to be insignificant.
- UCE of microplastics due to extreme weather events like floods or typhoons are not taken into account within the estimations of UCE_{wet}.
- UCE_{wet} may indirectly account for the proportions of microplastics that are deposited on land surfaces from numerous sources (atmospheric fallouts, mismanaged plastic waste, tire wear and road wear, and sewage sludge applied on agricultural lands) and simultaneously conveyed to the receiving waters through surface runoff.
- The fractions of microplastics that may not be carried along with surface runoff (in UCE_{wet}), for instance, those trapped in soil and removed through land sweeping are not taken into account in these estimations.
- Accidental releases of microplastics will not take place within the catchment.

The data were curated and processed using Microsoft Excel. QGIS ver. 3.22.11 was used for delineating the catchment and creating maps. Past and real-time weather information was obtained from the website of the Japan Meteorological Agency.



Remarks

- MP loads in inflow **(M_{in})**
  = {River MP concentration (μg/m^3) × River flow rate (m^3/day)} at catchment inlet
- MP loads in outflow **(M_{out})**
  = {River MP concentration (μg/m^3) × River flow rate (m^3/day)} at catchment outlet
- Controlled MP emissions conveyed through sewer lines **(CE_{in})**
  = {MP concentration (μg/m^3) × Flow rate (m^3/day)} of untreated wastewater × 365 days
- Controlled MP emissions exiting WWTPs **(CE_{out})**
  = {MP concentration (μg/m^3) × Flow rate (m^3/day)} of treated wastewater × 365 days
- Uncontrolled MP emissions in dry weather **(UCE_{dry})** $= \{(M_{out} - M_{in}) - \frac{CE_{out}}{365 \text{ days}}\} \times$ number of dry days per year
- Uncontrolled MP emissions in wet weather **(UCE_{wet})** $= \{(M_{out} - M_{in}) - \frac{CE_{out}}{365 \text{ days}}\} \times$ number of wet days per year
- Annual MP emissions without considering WWTP treatment $= CE_{in} + UCE_{dry} + UCE_{wet}$
- Annual MP emissions considering WWTP treatment $= CE_{out} + UCE_{dry} + UCE_{wet}$

Figure 5-2 Sources and transmission pathways of controlled and uncontrolled emissions of microplastics within the catchment
("MP" refers to microplastic and "WWTP" refers to wastewater treatment plant)

Table 5-3 Number and mass concentrations of microplastics in river water during dry days and WWTP influent and effluent

	Sampling location	Units of concentration	Concentrations of microplastics in different size clusters							
			10-40 μm	**40-70 μm**	**70-100 μm**	**100-300 μm**	**300-1,000 μm**	**1,000-2,000 μm**	**2,000-5,000 μm**	**Total (10-5,000 μm)**
River	Mikage bridge	Number (items/m^3)	3,681	2,991	1,150	460	0	0	1	8,283
		Mass (μg/m^3)	3	11	13	15	1	43	192	279
	Nishioh bridge (Catchment inlet)	Number (items/m^3)	3,809	816	204	340	0	1	0	5,170
		Mass (μg/m^3)	2	4	3	29	6	135	304	484
	Miyamae bridge (Catchment outlet)	Number (items/m^3)	12,987	5,405	2,102	976	6	6	5	21,487
		Mass (μg/m^3)	9	32	34	69	252	727	3,901	5,024
Wastewater treatment plants (WWTPs)										
WWTP - *A*	Inlet 1	Number (items/m^3)	500,612	500,612	166,871	166,871	90	50	50	1,335,156
		Mass (μg/m^3)	330	2,198	2,582	16,041	1,123	10,358	35,524	68,157
	Inlet 2	Number (items/m^3)	82,974	0	0	82,974	310	80	490	166,828
		Mass (μg/m^3)	85	0	0	6,416	2,459	10,182	649,878	669,020
	Outlet 1	Number (items/m^3)	5,340	3,560	890	890	0	0	0	10,680
		Mass (μg/m^3)	6	14	7	33	14	19	92	184
	Outlet 2	Number (items/m^3)	3,849	2,749	550	0	2	4	1	7,155
		Mass (μg/m^3)	4	16	8	0	21	310	673	1,032
WWTP - *B*	Inlet	Number (items/m^3)	291,793	250,306	83,435	124,922	200	65	270	750,992
		Mass (μg/m^3)	207	1,099	1,291	11,228	1,791	10,270	342,701	368,588
	Outlet	Number (items/m^3)	4,595	3,155	720	445	1	2	0	8,918
		Mass (μg/m^3)	5	15	7	17	17	164	382	608

5.3 Results and discussion

5.3.1 Comparison of magnitude and size composition of microplastics in sources of CE and UCE

The annual loads of microplastics from CE and UCE rely on their abundance in various relevant sources within the catchment, as well as the inflow and outflow during dry and wet weather. The river discharge increases by ~50% as the flow progresses from upstream to downstream, resulting in a ten-fold increment in the mass concentrations (four-fold increment in the number concentrations) in catchment outflow compared to the inflow (Figure 5-3a and Figure 5-3b). The treated effluents from WWTPs are considered a crucial point source of microplastics in urban rivers (Kataoka et al., 2019). However, in the present catchment, treated wastewater indicates relatively low concentrations compared to catchment outflow in both dry weather and wet weather, suggesting considerable microplastic inputs through diffused sources (Figure 5-3a and Figure 5-3b). The average mass concentrations of catchment inflow/outflow in wet weather were approximately increased by ~100-folds (numbers increased by ~50-folds) compared to the abundances in dry weather, due to the stormwater inputs (Figure 5-3a and Figure 5-3b). However, the runoff discharges and the subsequent microplastic inflows may largely vary upon rainfall characteristics for different rainfall scenarios as shown in Chapter 4.

The untreated wastewater conveyed through the local sewer system denotes 70 times higher mass concentrations (40 times higher number concentrations) compared to catchment outflow in dry weather. Nevertheless, in wet weather, the outflow is as concentrated as untreated wastewater (Figure 5-3a and Figure 5-3b), indicating adverse pollution effects by runoff emissions equivalent to the direct discharges of untreated wastewater. In agreement with a few past studies, higher microplastic abundances have been observed in urban stormwater runoff compared to treated wastewater effluents in several catchments, as further explained in Section 5.3.2 (Bailey et al., 2021; Cho et al., 2023).

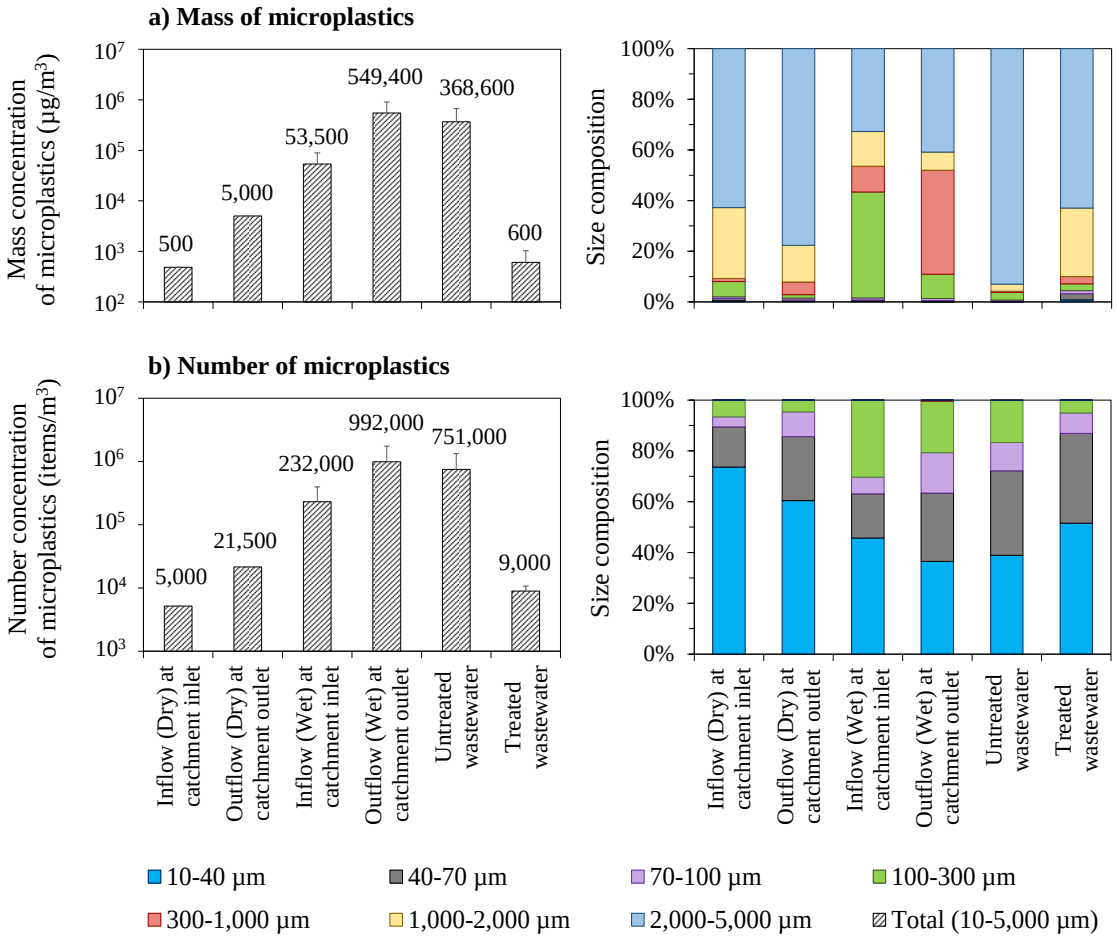


Figure 5-3 The average concentrations of microplastics in river water and wastewater and the respective particle size compositions
(The concentrations are indicated in terms of a) mass and b) number of microplastics at catchment inlet and outlet (river water), and in untreated and treated wastewater (influent and effluent of wastewater treatment plants); Error bars represent the standard deviation of the average concentrations).

Overall, the size composition of microplastics in CE and UCE was dominated by particles larger than 2,000 µm in terms of mass and particles smaller than 40 µm in terms of number (Figure 5-3a and Figure 5-3b). However, microplastics in the size clusters 100–300 µm and 300–1,000 µm in river water were heavily impacted by rainfall and runoff events (Figure 5-3) as shown by their higher proportions in catchment inflow (100–300 µm: ~40%) and outflow (300–1,000 µm: ~40%) in wet weather. Similar compositions have been noted in the road runoff sampled in Tokyo (Japan) and river water samples from the Qin River, China, following a rainfall event (Sugiura et al., 2021; Wei et al., 2022). This can be explained by the higher proportions of microplastics in the size clusters 125–300 µm and 300–1,000 µm detected in the road dust sampled from Japan and

overseas (Morioka et al., 2023; Yukioka et al., 2020), which are potentially mobilized along with surface runoff during rainfall events.

5.3.2 Annual microplastic emissions of the catchment and the comparative contribution of CE and UCE

5.3.2.1 Annual microplastic emissions without considering WWTP treatment

When treatment operations by WWTP are disregarded, the catchment releases 269.1 tons (range: 89.1–335.5 tons) of microplastics annually, constituting UCE_{dry} (2.1 tons (range: 0.9–2.9 tons); 0.8% (range: 0.6%–1.9%)) < CE_{in} (56.9 tons; 21.1% (range: 17.0%–63.8%)) < UCE_{wet} (210.1 tons (range: 31.4–275.8 tons); 78.1% (range: 35.2%–82.2%)) (Figure 5-4). This trend means that only one-fifth of the total microplastic releases are attributed to untreated wastewater emissions, whereas the rest is extensively due to uncontrolled discharges, particularly on wet days. If the annual emissions are split between wet and dry seasons, UCE occupies 92.3% (range: 64.2–94.0%) in wet weather (UCE_{wet}); but 5.1% (range: 2.3–6.7%) in dry weather (UCE_{dry}), where untreated wastewater dominates the total emissions (CE_{in}: 94.9% (range: 93.3–97.7%)). Overall, the particle size distribution of the annual microplastic stocks indicates increasing masses with increasing particle size (Figure C–3). Similar to the source composition of total microplastics, CE_{in} shares nearly one-third of the microplastic loads in the size clusters smaller than 70 µm and larger than 2,000 µm (Figure C–4). Additionally, UCE_{wet} represented 99.5% of the microplastic loads in 300–1,000 µm size cluster, as runoff inflows seem to boost microplastics of this size range (Figure C–4) as previously explained in Section 5.3.1.

The massive discharge of microplastics through UCE_{wet} can be attributed primarily to runoff inflows and wet depositions of atmospheric microplastics (Allen et al., 2019; Horton & Dixon, 2018). While microplastic data is lacking within the context of the present study area to clarify the discrete contribution of these two sources on UCE_{wet}, the evidence from UCE_{dry} inferred low involvement of wet depositions compared to microplastic inputs through surface runoff. Moreover, our estimate for UCE_{wet} also compensated for the fractions of microplastics intercepted and retained on the soil while mobilizing along with the runoff and further for those subjected to sedimentation and resuspension due to the compounding hydrodynamics along the flow paths (Hurley et al.,

2018; Nizzetto, Bussi, et al., 2016).

The case where we disregarded the WWTP treatment can also represent the scenario of a low-income economy, where untreated wastewater would be freely released to the environment along with uncontrolled emissions in the absence of systematic wastewater management practices. United Nations reported that over 80% of global wastewater is released to the environment with zero treatment (UNESCO, 2017), exhibiting a crucial source of microplastics in freshwater environments. Nevertheless, the present evidence suggested more severe impacts by uncontrolled stormwater discharges, even within the context of well-developed urban agglomerations. The annual flow volume introduced to the river through surface runoff (140 million m^3) is also twice that of untreated wastewater (80 million m^3), resulting in relatively high microplastic inputs through runoff inflows.

5.3.2.2 Annual microplastic emissions considering WWTP treatment

With the intervention of wastewater treatment, almost all microplastics conveyed through separate sewer systems are treated at an efficiency of 99.8%. Following treatment, the treated effluent occupied only 0.1% (range: 0.0–0.3%) of the annual microplastic loads released to the river (212.4 tons/annum; range: 32.4–278.7 tons/annum), and the rest was almost entirely occupied by runoff discharges (UCE_{wet} = 98.9%; range: 96.8–98.9%) (Figure 5-4). Individual size clusters also indicated similar distribution of microplastic source composition, following WWTP treatment (Figure C–4). In wet weather, WWTP treatment contributes less significantly to abating microplastic pollution of the river due to relatively high microplastic fluxes through runoff (Figure 5-4). On the contrary, WWTPs effectively regulate the dry weather emissions of microplastics by bringing down CE from 94.9% (range: 93.3–97.7%) to 3.2% (range: 2.4–7.2%); concurrently, microplastic pollution of the river network during dry weather is predominated by direct atmospheric depositions on the river surface (Figure 5-4). This evidence further manifested a prominent involvement of uncontrolled emissions than treated wastewater discharges to the microplastic pollution of freshwater environments, not just in wet weather but also in dry weather.

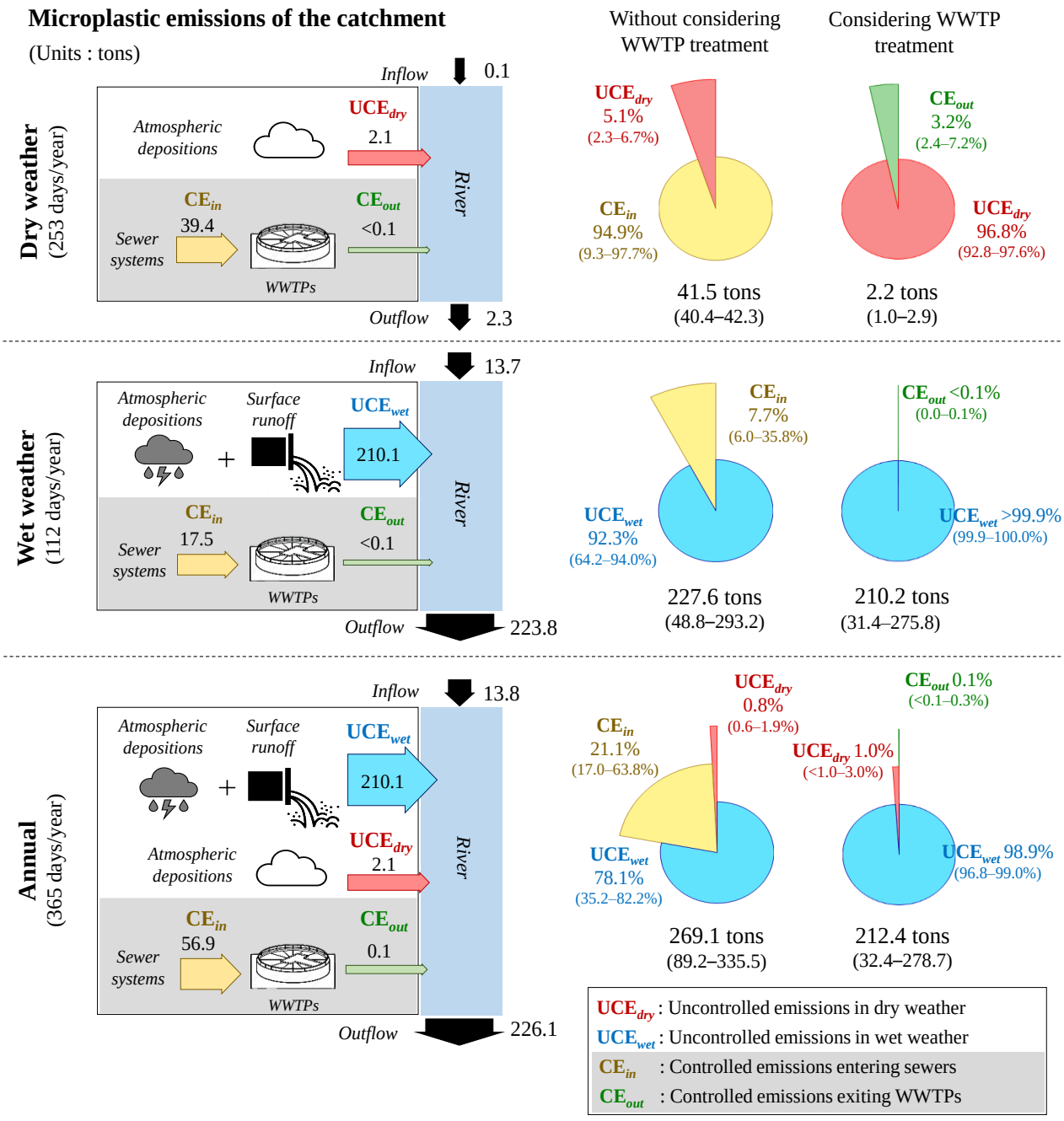


Figure 5-4 Microplastic emissions of the catchment considering and without considering treatment at the wastewater treatment plants (WWTPs)
(A range of possible values for each emission component of microplastics are indicated within parenthesis. Refer to Figure C–4 for the results of varying size clusters).

Previous studies that estimated microplastic emissions from urban agglomerations rarely clarified distinctions between the proportions of controlled and uncontrolled disposes of microplastics. A recent study on an urban catchment in Shanghai megacity, China, reported that 54% of the total microplastic emissions are directed to WWTPs while the rest (46%) are discharged to the receiving waters (Chen et al., 2022). The fractions of microplastics conveyed to WWTPs are relatively high in this study compared to ours (CE_{in} = 21.1%; range: 17.0–63.7%), probably due to the involvement of combined sewer systems that intercept wastewater and stormwater runoff. Apart from this, several studies hinted at a pronounced involvement of surface runoff in the microplastic pollution of aquatic environments compared to WWTP effluents in support of the present results. For instance, microplastics discharged in combined sewer systems were six times higher than the discharges via WWTP effluent in Raritan River, USA (Bailey et al., 2021). Additionally, microplastics conveyed through WWTP effluent and combined sewer overflows (CSOs) accounted for 25% and 62%, respectively, in the Baltic Sea (Schernewski et al., 2021). Furthermore, stormwater systems contributed to 43% of microplastic stocks in the Warnow estuary, Germany compared to 6% of CSO emissions and 1% of WWTP effluent emissions (Piehl et al., 2021).

While these studies (together with a few more listed in Table 5-1 implied lower proportions of microplastic releases to the receiving waters through surface runoff relative to the present evidence (for CE_{out}), a recent study revealed comparable results indicating 99% of the total microplastic loads ascribed to stormwater runoff and 1% to WWTP effluent in a tributary river to Nakdong River, South Korea (Cho et al., 2023). Interestingly, this study also employed a comprehensive analysis of microplastic inputs through runoff (in a separate-sewer catchment) similar to the present case, whilst other studies involved limited sampling in wet weather (involving combined sewer systems). Additionally, our findings are consistent with the model-based estimations for Charleston Harbor, USA, where WWTP effluents accounted for less than 0.1% of the annual microplastic emissions to surface waters, resulting in 0.34–0.68 g/person/year of microplastic emissions, exclusively through treated wastewater effluents (present estimations = 0.43 g/person/year) (Conley et al., 2019).

Table 5-4a compares microplastic loads discharged through runoff per unit area of the catchments investigated by Cho et al. (2023) and the present study, considering diverse rainfall conditions. Overall, the present estimations are comparatively high but

varied within the same order (particularly for low and high-intensity rainfalls) in the two studies. The higher rates of emissions in the present study could be credited to the disparities in land use, topography, waste management practices, and methods involved in the analyses. This comparison demonstrates that microplastic discharges are highly varied upon rainfall characteristics. Our data for moderate and heavy rainfall events suggested that high-intensity rainfalls in conjunction with high antecedent dry days give rise to higher fluxes of microplastics (Table 5-2); therefore, high-frequency sampling at rainfall episodes with varying characteristics is vital to capture the true magnitude of microplastic transmissions through runoff emissions. Although the total number of rainy days occupied ~30% of an average year in the study area (112 days/year), this period accounted for ~99% of the annual microplastic discharges in the river network (Figure 5-4). Additionally, the highest contribution to the wet weather emissions was from moderate and heavy rainfall episodes (96%), although such events occur less frequently (18% of the year) compared to light rainfalls (light: 48 days/year, 4%; moderate: 35 days/year, 34%; heavy: 29 days/year, 62%). Therefore, sampling in wet weather should sufficiently account for moderate to heavy rainfall events for a representative analysis of microplastic emissions.

5.3.3 Surface area-normalized emissions and insights on microplastic mitigation in urban catchments

This study highlighted the importance of regulating microplastic emissions through runoff in order to abate microplastic pollution of the receiving waters in urban agglomerations. While it is imperative to employ effective stormwater management strategies to tackle this issue, source prevention of microplastic emissions is more rational, considering the high costs involved with stormwater infrastructure. Proper waste management at the source of generation would be a great way to reduce microplastic accumulation on the land surface and thereby reduce its flushing off through runoff. Nonetheless, the present findings indicated higher microplastic emissions for a well-planned urban catchment in Japan, where mismanaged plastic waste (MMPW) is maintained at a very low level (0.28 kg/person/year) compared to many developing as well as developed countries (Meijer et al., 2021).

Table 5-4 Comparison of the microplastic emissions from the present study area with the previous reports

a) Loads of microplastics discharged from different catchments during different rainfall events

Study area	Total rainfall (mm); Duration (h) of rainfall event	Antecedent dry days	Average rainfall intensity of the event (mm/h)	Microplastic load discharged per event (kg/km^2)	Reference
A sub-catchment of Kamo River, Japan	6.0 mm; 5 h	3	0.3	0.90	This study
	24.0 mm; 7 h	14	3.4	9.70	
	52.0 mm; 7 h	2	7.4	21.30	
A sub-catchment of Nakdong River, South Korea	27.0 mm; 17 h	2	1.6	0.80	Cho et al., 2023
	2.2 mm; 1 h	18	2.2	0.03	
	61.6 mm; 12 h	1	5.1	15.71	

b)* Surface area-normalized annual microplastic loads discharged into the receiving waters from different selected catchments worldwide

River basin / sub-catchment	Annual microplastic load (tons/annum)	Catchment area (km^2)	Surface area-normalized annual microplastic emissions (tons/ km^2 /annum)	Mismanaged plastic waste generation (kg per capita) (Meijer et al., 2021)	Reference
Danube River, Austria	1,533	801,463	0.002	0.32–2.69	Lechner et al., 2014
Lake Geneva, Switzerland/France	55	7,999	0.007	0.43	Boucher et al., 2019
Nakdong River, South Korea	53–118	21,588	0.002–0.005	0.24	Eo et al., 2019
Pearl River, China	15,963	450,000	0.035	8.56	Fan et al., 2019
Lianfang river, China	188	528	0.356	8.56	F. Xia et al., 2023
Huangpu River, China	3,207	6340	0.506	8.56	Chen et al., 2022
Kamo river, Japan	212	280	0.757	0.28	This study
Seine River Basin, France	924–1,675	889	1.039–1.884	0.43	Treilles et al., 2022

* Refer to Table 5-1 for further global reports on annual microplastic emissions from urban catchments.

Table 5-4b compares microplastic loads entering the receiving waters from several urban catchments worldwide by accounting for the differences between the catchment areas (surface area-normalized microplastic emissions). While most of these catchments are located in developed countries, the relevant data are scarce from developing countries for a better comparison. Interestingly, the degree of plastic pollution in a majority of these past study areas did not always justify the annual microplastic releases owing to the limited sampling involved during rain. For instance, the basins of Sein River (France) and the sub-catchment of Kamo River (present study area) indicated the highest annual fluxes of microplastics from a unit catchment area (1.039–1.884 tons/km^2/year and 0.757 tons/km^2/year, respectively), notwithstanding the low levels of MMPW generation. The relatively high microplastic inputs from the catchments of Huangpu River (0.506 tons/km^2/year) and Lianfang River (0.356 tons/km^2/year) from China may be ascribed to the higher rates of MMWP generation (8.56 kg/person/year), yet catchment of Pearl River, the third largest river in China showed one-order of magnitude lower microplastic discharges (0.035 tons/km^2/year). It is noteworthy that the three studies indicating the highest microplastic emissions (basins of Kamo, Sein, and Huangpu Rivers) involved extensive sampling during rain, whilst the catchments of the Pearl River and the Lianfang Rivers showed otherwise.

While the low pollution levels in South Korea may reflect the low emissions from the Nakdong River basin (0.002–0.005 tons/km^2/year), this study was also devoid of adequate sampling in the rain but rather considered the seasonal differences in the plastic emissions. Lake Geneva basin, Switzerland/France (0.007 tons/km^2/year) indicated the second lowest emissions notwithstanding the runoff and CSO sampling involved. These low quantities were credited to the extensive sinking and sedimentation of microplastics within the lentic water environments in lakes (Boucher et al., 2019). The lowest emissions were noted for the Danube River basin (0.002 tons/km^2/year), which spans through ten countries and marks the second-longest river in Europe, once again indicating an underestimation caused by the low representation of runoff discharges. These comparisons manifest that the influence of untreated runoff discharges on the microplastic pollution of the urban freshwaters has been underrated so far on the grounds of inadequate sampling. Given the extensive plastic waste mismanagement in developing countries, especially in the Asian region (Jambeck et al., 2015; Meijer et al., 2021), much higher microplastic releases can be speculated for the respective catchments if the fluxes

are estimated based on sufficient data accommodating wet weather. Such understanding is a prerequisite to elucidate the directions of microplastic pollution mitigation at the regional scale.

For urban clusters like the present study area, where somewhat satisfactory plastic waste management is already in place, stormwater management measures may contribute to a significant reduction in microplastic pollution. Within the context of Japan, the existing sewer systems are rapidly upgraded to separate sewer equivalents by providing storage trunks to retain a part of the stormwater during heavy rain so that it can be treated later at the WWTPs during dry days. Furthermore, alternative measures involving stormwater treatment facilities, retention ponds, permeable pavements, and rain gardens are also constructed in some major cities. Moreover, green infrastructure is becoming gradually recognized in stormwater management at the regional scale. These measures have proven to abate flooding and pollutant surcharges during storm events. Nonetheless, the performance of these systems has not been investigated to date on their capacity to reduce microplastics. At least the present findings suggested that the existing measures viz., separate sewer systems, are inadequate in the absence of simultaneous treatment measures for stormwater. Future research may explore low-cost methods for removing microplastics from urban runoff, considering the low-income economies of the developing regions where plastic pollution is foremost.

5.4 Conclusions

This study employed a conservative mass balance approach to quantify the annual microplastic emissions of an urban catchment in Japan where separate sewer systems are well-established. We established that only one-fifth of the total microplastics (size range: 10–5,000 µm) released from a typical urban catchment is intercepted and removed by WWTPs, and the rest is freely disposed to the receiving river. Following effective treatment at WWTPs (99.8% removal rates), the total microplastic discharges to the river constitute 98.9% (range: 96.8–99.0%) of emissions dominated by unmanaged surface runoff. The rest is derived from atmospheric depositions in dry weather (average: 1.0%; range: <1.0–3.0%) and treated wastewater effluents (average: 0.1%; range: <0.1–0.3%). This study established that WWTP effluents contribute to the microplastic pollution of river systems to a lesser extent than diffused sources in both dry (atmospheric depositions) and wet weather (runoff discharges). Additionally, we pointed out that microplastic

emissions via surface runoff may inflict more severe pollution effects than untreated wastewater, even in well-developed urban agglomerations.

Future studies may consider the frequent sampling of microplastics during the onset of rainfall events, prioritizing moderate to heavy rainfall episodes (occur during 18% of the year) for a realistic appraisal of microplastic pollution induced by surface runoff. Furthermore, it is prudent to adopt surface area-normalized microplastic emissions from an urban catchment when formulating microplastic interventions, particularly for developed cities. In the context of a high-income economy, free releases of microplastics can be minimized through treatment measures for stormwater. Such measures should be of sufficient capacity to intercept 300–1,000 μm-sized microplastics that are surged into receiving waters through surface runoff.

CHAPTER 6. Conclusions and recommendations

6.1 Conclusions

This study aimed to clarify the contribution of surface runoff to the microplastic pollution of a receiving river associated with an urban catchment, which was sequentially achieved through three key objectives. For this, the primary river network of the metropolitan Kyoto City in Japan consisting of the Katsura and Kamo Rivers was investigated by sampling for a wide size range of plastic debris in dry and wet weather. The three objectives introduced new insights on the occurrence, spatiotemporal distribution patterns, rainfall-driven emission dynamics for (micro)plastics based on their particle size. Such information would be useful when planning interventions for microplastic pollution of urban rivers, particularly through surface runoff. Moreover, this study added to clarifying the contribution of Japan to the global pollution of microplastics in river systems and its consequences on the North Pacific Ocean and adjoining maritime zones. The overall conclusions derived for the three key objective of the study are as follows.

Firstly, this study presented new evidence on the characteristics of plastic pollution of an urban river network based on the simultaneous analysis of microplastic particles and microplastic fibers (MPFs; 10–5,000 µm), and mesoplastics (5,000–25,000 µm) under steady flow conditions in dry weather. In terms of the numerical abundance, microplastics smaller than 300 µm occupy 99.94% of the particles in the total size range of 10–25,000 µm, where 50% is smaller than 40 µm. On the contrary, the mass-based abundance indicated 96% occupancy by particles larger than 1,000 µm. It should be noted that the method used for estimating mass of microplastic particles throughout this study might have produced approximately 4 times higher masses than the actual/measured masses, assuming an insignificant contribution to the total mass by particles smaller than 300 µm. Additionally, we exemplified that minimum particle size would be a useful indicator to compare microplastic pollution levels globally and revealed moderate plastic pollution levels in Japanese urban rivers compared to riverine environments worldwide.

This study further provided the first insights on the real-time dynamics and mobilization characteristics of microplastic particles and MPFs (10–5,000 µm) in urban rivers during the occurrence of rainfall-runoff events with different characteristics. We

demonstrated that numerous rainfall characteristics may act synergistically to influence the size-specific emission patterns for microplastics. For instance, microplastics as small as 10–40 µm are rapidly mobilized at lower rainfall intensities, indicating first-flush effects (discharges with the initial 20% of the river flow during rain), whereas those larger than 2,000 µm are discharged at higher rainfall intensities (discharges with river flow volumes exceeding 45%). The results indicated that runoff inflows may increase the loads of microplastics transmitted through river water by 4–110-folds compared to dry weather. Although riverine MPFs are significantly high in abundance compared to microplastic particles during dry weather, they are trivially impacted by the runoff inflows.

Lastly, this study resolved the relative contribution of uncontrolled emissions such as surface runoff (and atmospheric depositions), and controlled wastewater emissions to the annual microplastic releases of urban catchments (size range: 10–5,000 µm), employing a mass balance approach. Out of the total annual microplastic emissions of a well-developed urban catchment like the present study area (average: 269.1 tons/annum; range: 89.2–335.5 tons/annum), nearly one-fifth (average: 21.1%; range: 17.0–63.8%) is intercepted and removed by WWTPs. Accordingly, the treated wastewater effluents occupy only 0.1% (range: <0.1–0.3%) of the total microplastics released to the receiving river network, while the rest is predominantly occupied by surface runoff (average: 98.9%; range: 96.8–99.0%) and insignificantly by atmospheric depositions in dry weather (average: 1.0%; range: <1.0–3.0%). This demonstrated that treated wastewater effluents contribute to the microplastic pollution of river systems to a lesser extent than diffused sources in both dry and wet weather. Additionally, microplastic emissions via unregulated surface runoff may inflict more severe pollution effects than untreated wastewater.

While interventions for microplastic pollution through surface runoff have been scarcely investigated in the existing research, we showed that intercepting the initial 40% of the runoff inflows into the rivers may abate microplastic contamination of urban rivers to a significant extent. Furthermore, we elucidated the opportunity to predict the dynamics of microplastics using typical non-point source pollutants (e.g., suspended solids) and the possibility for size-targeted mitigation of microplastics by optimizing the existing stormwater management mechanisms. Additionally, it was revealed that moderate to heavy rainfall periods which occupy only 18% of the total year (within Japan) is crucial for controlling ~95% of the annual microplastic emissions into urban rivers. The importance of adopting high-frequency sampling for a realistic assessment of riverine

microplastic pollution caused by surface runoff was emphasized throughout this study. Lastly, we highlighted the relevance of employing surface area-normalized emissions (~0.8 tons/km^2/annum for present catchment) as an indicator to compare the impact of unmanaged surface runoff emissions globally. Such measures would be beneficial when formulating interventions for microplastic pollution, particularly in the developed cities.

In summary, the new findings of the study are as follows:

In a developed urban catchment facilitated with separate sewer systems,

- approximately one-fifth of the annual microplastic emissions (in the size range of 10–5,000 µm) are captured by WWTPs.
- almost 99% of the annual microplastic emissions into urban rivers are caused by surface runoff.
- untreated surface runoff imposes more severe microplastic pollution compared to untreated wastewater even in the existence of satisfactory plastic waste management practices.
- the period of moderate to heavy rainfall events (average rainfall intensities exceeding 2.5 mm/h) which occupies only 18% of the year is crucial for controlling microplastic pollution caused by surface runoff.
- intercepting and treating the initial 40% of the surface runoff that is freely discharged into the environment may reduce microplastic pollution of urban rivers at least by 50%.
- very small microplastics (10–40 µm) are rapidly mobilized at lower rainfall intensities (with the initial 20% of the runoff inflows), whereas those larger than 2,000 µm are discharged at higher rainfall intensities (with runoff flow volumes exceeding 45%).
- the dynamics of riverine microplastic emissions during rain can be predicted with those of suspended solids.
- microplastic fibers in river water are less impacted by rain and subsequent surface runoff, compared to microplastic particles.

6.2 Recommendations for future research

This study involved analysis of microplastics down to 10 µm during both dry and wet weather, and mesoplastics only in dry weather. However, large plastic debris (e.g., mesoplastics and macroplastics) are primarily introduced to river environments through surface runoff, and may crumble into smaller pieces in the long run. Therefore, it is imperative to investigate their mobilization through runoff inflows for effective pollution control of river systems.

Further research is needed from developing cities to explicate the regional contribution to runoff-driven microplastic pollution of the global river systems. In developed countries, the existing stormwater management measures should be assessed for their capacity to retain microplastics of various size clusters, taking into account the similarities between the emissions characteristics of microplastics and typical non-point source pollutants. In the meantime, low-cost solutions should be explored for microplastic emission control via stormwater. Future research may also investigate the build-up and wash-off processes of microplastics under different rainfall scenarios.

Since conventional analytical methods of microplastics may not be suitable for MPFs, the future studies may investigate novel analytical approaches which facilitate simultaneous identification of physical and chemical characteristics of MPFs. Although our mass balance approach did not facilitate the quantification of annual emissions of MPFs, it is important to clarify the source contribution to MPF stocks in rivers, considering their omnipresence and ecotoxicological risks. This study indicated insignificant impact of runoff events on MPF fluxes in rivers associated with separate sewer systems. Nevertheless, it would be interesting to investigate MPF emissions through runoff in combined sewer areas to distinguish the effectiveness of separate sewer systems in controlling MPF emissions into receiving waters. Moreover, it is important to quantify microplastic inputs into freshwater in the forms of wet (atmospheric) depositions.

The disparities in the methods used for sampling, extraction, identification and quantification of microplastics in different studies may limit the comparability of data; therefore, standardized protocols need to be established for microplastics in riverine environments, incorporating high-frequency sampling approaches for rainfall-runoff events. More importantly, methods should be developed for accurate estimation of the mass of microplastics. Finally, appropriate policies, regulations and abatement measures

needs to be developed for systematic management of microplastic pollution induced by surface runoff, through national and global collaborations.

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Appendix A Supplementary Information for Chapter 3

Table A–1 Details of the sampling stations

Sampling station	Coordinates of sampling station	Flow velocity (m/s)	Discharge (m^3/s)	Discharge (m^3/day)
Mikage bridge (R1)	35.03427, 135.77463	0.12	1.93	166,925
Aoi bridge (R2)	35.03212, 135.77016	0.13	1.33	115,016
Nishikyogoku bridge (R3)	34.99464, 135.71680	0.42	0.46	40,159
Nishioh bridge (R4)	34.99393, 135.70947	0.78	10.16	877,824
Kuze bridge (R5)	34.96489, 135.72224	0.08	17.40	1,503,360
Kyogawa bridge (R6)	34.94644, 135.74054	0.79	11.59	1,001,082
Miyamae bridge (R7)	34.90805, 135.71599	0.31	30.60	1,848,960

Table A–2 Spectra of some polymers frequently tested with ATR-FTIR

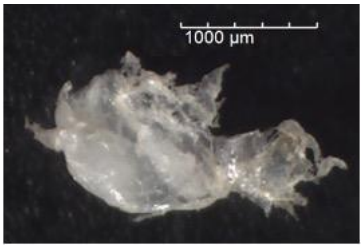
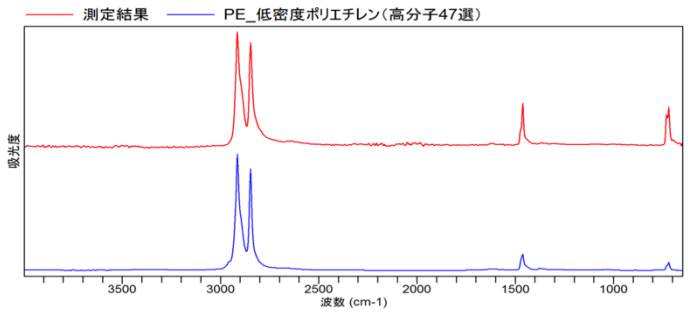
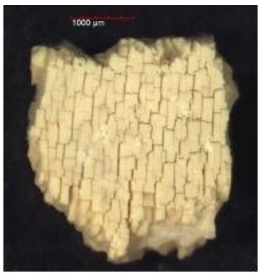
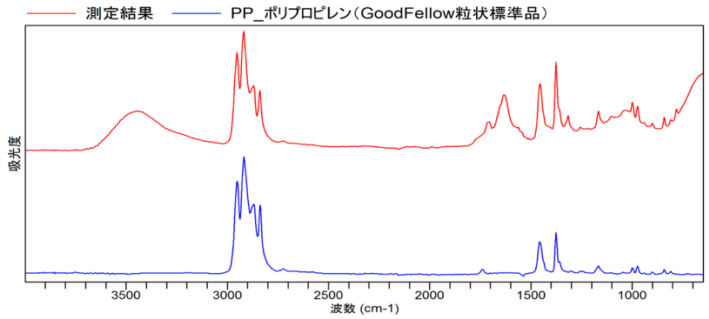
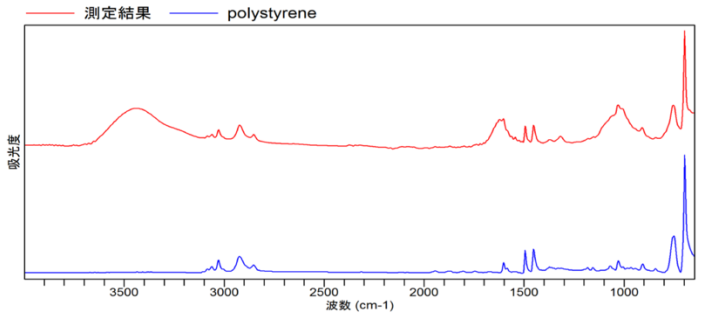
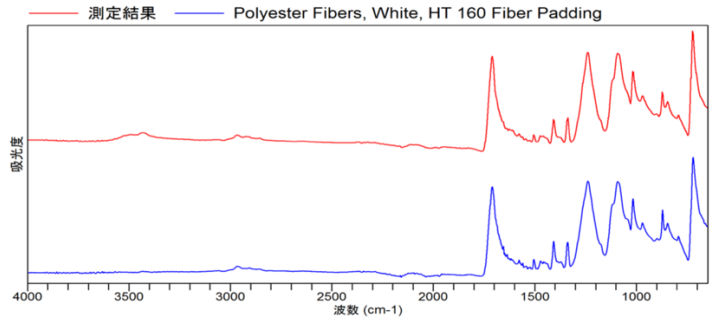
Polymer Type	ATR-FTIR spectrum
Polyethylene (PE) 	
Polypropylene (PP) 	
Polystyrene (PS) 	
Polyethylene terephthalate (PET) 	

Table A–2 Spectra of some polymers frequently tested with ATR-FTIR (continued)

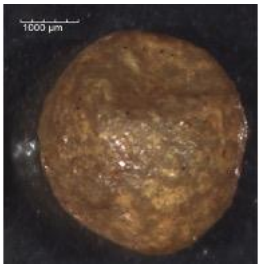
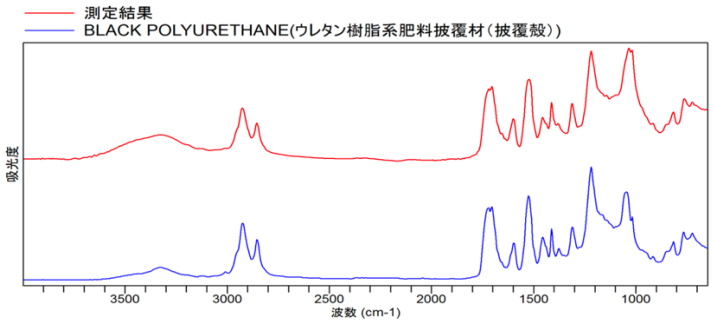
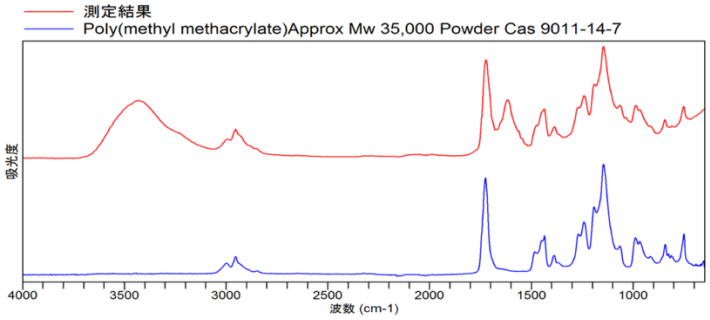
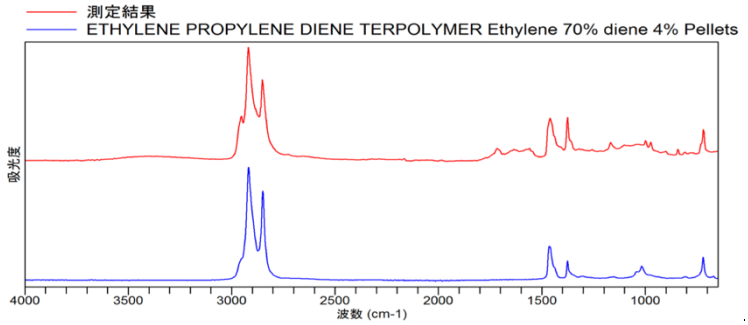
Polymer Type	ATR-FTIR spectrum
Polyurethane (PUR) 	
Poly (methyl methacrylate) (PMMA) 	
Ethylene-Propylene-Diene-Monomer (EPDM) 	

Table A–3 Spectra of some polymers frequently tested with µ-FTIR

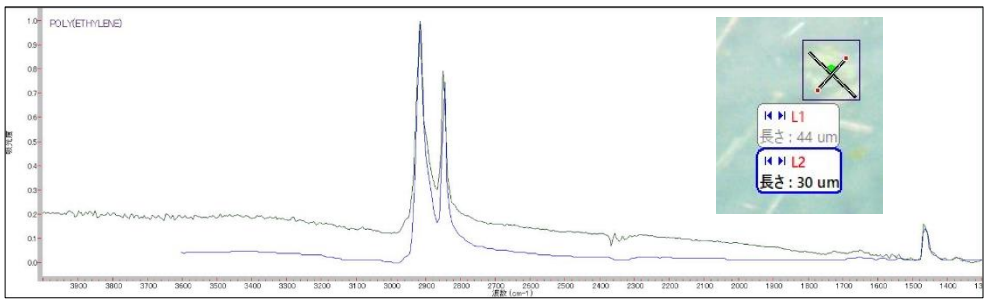
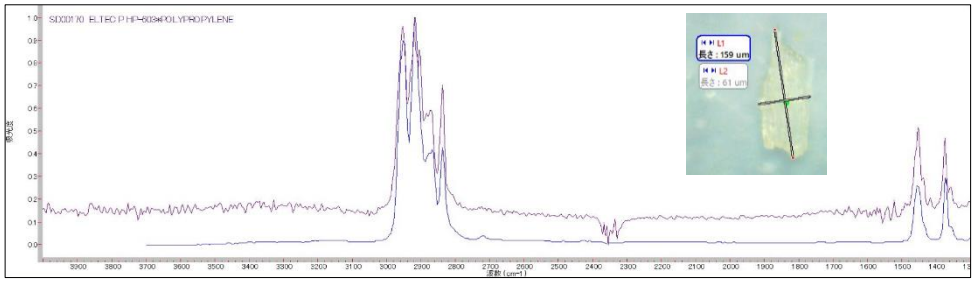
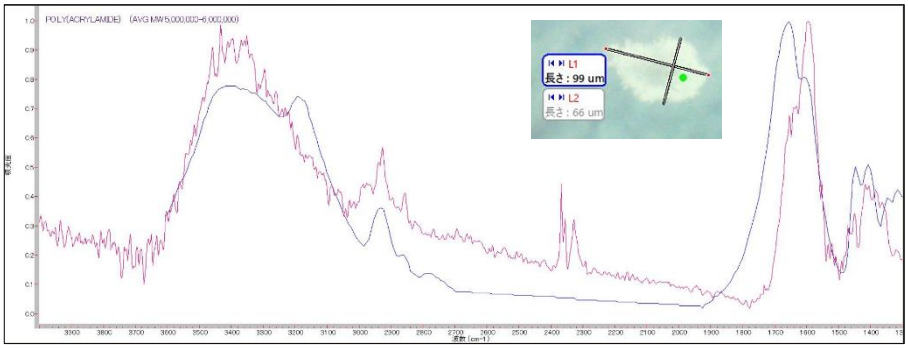
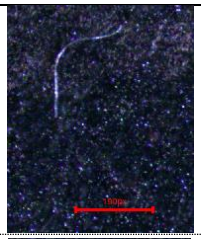
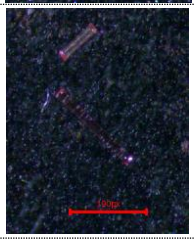
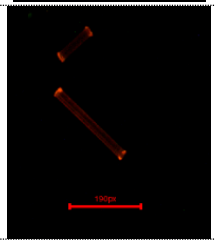
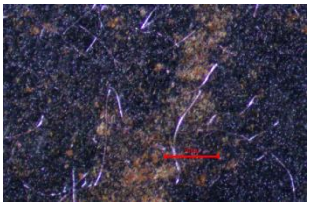
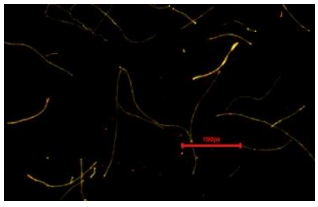
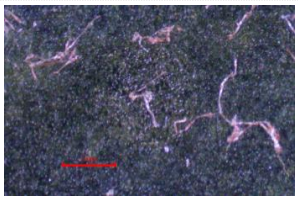
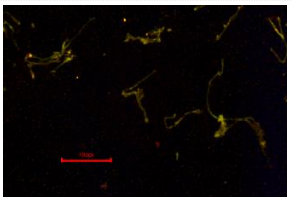
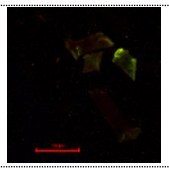
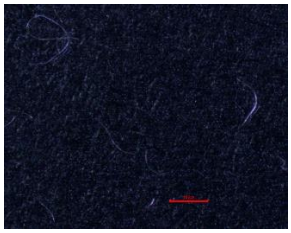
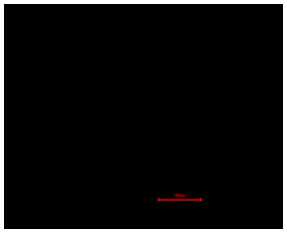
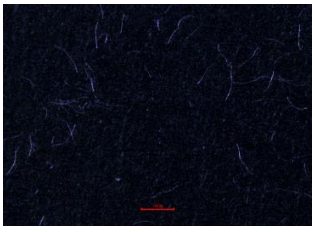
Polymer Type	Image of plastic particle and respective µ-FTIR spectrum
Polyethylene (PE)	
Polypropylene (PP)	
Polyacrylamide (PAM)	

Table A–4 Microscopic observations of Nile red-stained MPFs of known polymers and non-plastic fibers

Type	Observations by Stereomicroscope	Observations by Fluorescence microscope	Colour of fluorescence
PET			Red
Nylon			Red
Acrylate			Yellow
PE			Green
PP			Green
Cotton			-
Wool			-

Text A–1. Validation of the method of calculating mass of plastic particles

This study employed a method introduced by Cózar et al. (2014) (referred to as *"Method 1"*) to estimate the mass of microplastics in river water samples. Apart from that, the masses were estimated using another method proposed by Simon et al. (2018) (referred to as *"Method 2"*) which is widely applied in microplastic research. The calculated masses by *Method 1* and *Method 2* were then compared with the actual masses measured using an electronic balance to validate the present estimation method (see Table A–5). The calculation methods determine the mass of plastic particles by multiplying the volume of each particle by its respective polymer density. The method of calculating particle volume varies between *Method 1* and *Method 2* as follows.

***Method 1* by Cózar et al., 2014**

Volume of plastic fragments/films = $\frac{4}{3}\pi r^3 \alpha$

Where,

$$r = \frac{1}{2} \times \left(\frac{\text{Long dimension + Short dimension}}{2}\right)$$

α = Shape factor (0.1 for fragments and films, and 1 for spheres)

Volume of plastic fibers = $\pi r^2 L$

Where,

r = Diameter of the fiber

L = Length of the fiber

***Method 2* by Simon et al., 2018**

Volume of plastic particle = $\frac{4}{3}\pi abc$

Where,

a = Long dimension/2

b = Short dimension/2

$c = 0.67 \times b$

Volume of plastic fibers = $\pi r^2 L \times 40\%$; (r and L are defined above)

In general, the measured masses are lesser than those calculated by *Method 1* and *Method 2*, specially for mesoplastics (5–25 mm) and microplastics in the size range of 300 µm – 5 mm. For mesoplastics, the masses estimated by *Method 1* would be 7.5 ± 5.5 times higher than the measures values (correlation between measured and calculated masses (R^2) = 0.61), whereas the masses estimated with *Method 2* would be 29.6 ± 24.3 times higher (R^2 = 0.37). Similarly, for 300 µm – 5 mm microplastics, the estimated masses by *Method 1* would be 4.3 ± 4.5 times higher than the measured masses (R^2 = 0.88), whereas the same for *Method 2* would be 11.4 ± 11.7 times higher than the measured masses (R^2 = 0.95). However, for microplastics particles in the size range of 1–5 mm, the masses calculated by *Method 1* would be almost half the measured masses (0.5 ± 0.4; R^2 = 0.98) whilst the estimations by *Method 2* would be comparable (1.3 ± 0.9 times higher; R^2 = 0.91). Overall, the deviation of the calculated masses from the measured masses are lesser for *Method 1* than *Method 2*.

Table A–5 Comparison of the calculated masses of plastic samples by *Method 1* and *Method 2* with the respective measured masses

Particle size		Measured mass (g)	Cózar et al., 2014 **(Method 1)**		Simon et al., 2018 **(Method 2)**	
			Calculated mass (g)	Calculated mass / Measured mass	Calculated mass (g)	Calculated mass / Measured mass
5–25 mm (N_1=11; N_2=321) [a]	Min	<0.001	0.008	277.7	0.042	1391.3
	Max	0.936	5.172	5.5	25.080	26.8
	Average	0.161	1.214	7.5	4.769	29.6
	SD	0.329	1.812	5.5	7.998	24.3
1–5 mm (N_1=14; N_2=864) [a]	Min	<0.001	0.001	8.0	0.005	40.1
	Max	4.856	2.080	0.4	4.410	0.9
	Average	0.368	0.202	0.5	0.496	1.3
	SD	1.292	0.549	0.4	1.189	0.9
300 µm – 5 mm (N_1=14; N_2=1,318) [a]	Min	<0.001	<0.001	1.4	<0.001	3.1
	Max	0.037	0.189	5.2	0.452	12.3
	Average	0.006	0.026	4.3	0.070	11.4
	SD	0.010	0.050	4.8	0.120	11.7

[a] *"N_1" represents the number of plastic samples involved whereas "N_2" represents the number of plastic particles contained in those samples*

This comparison shows that the empirical equations may overestimate the masses of larger mesoplastics more, compared to microplastics. This could be due to the porosity of large plastic particles in the environmental samples which is not taken into account during the calculation of mass. The relatively higher deviation of estimated masses from

the measured masses in the size range of 300 µm – 5 mm could be attributed to the errors involved with measuring smaller masses with the electronic balance, as well as measuring the dimensions of smaller particles manually under microscopic view. Overall, the empirical methods seem to be more applicable for particles in the size range of 1–5 mm which occupy 89% of the total mass of microplastic particles in the size range of 10 µm – 5 mm.

Considering the lesser deviations and higher correlations between the measured and calculated data, *Method 1* is considered to be relatively more suitable for estimating the mass of plastic particles in the present study than *Method 2*.

Table A–6 Results of blank tests

Type of sample	Blank test 1	Blank test 2
Mesoplastics (5–25 mm)	0 particles	0 particles
Large microplastics (300 µm – 5 mm)	0 particles	0 particles
Small microplastics (10–300 µm)	0 particles	0 particles
Microplastic fibers (10 µm – 5 mm)	22 fibers	17 fibers

Table A–7 Results of recovery tests

Type of sample	Method of analysis	Type of standard particles used and details of spiked samples	Recovery
Large microplastics (300–5,000 µm)	ATR–FTIR	Polyethylene beads (Diameter: 850–1,000 µm) *Cospheric*	100%
Small microplastics (10–300 µm)	µ–FTIR	Polystyrene beads (Diameter - 30 µm; Particle density - 1.05 g/cm^3) *Thermo Fisher Scientific*	71%
Microplastic fibers (10–5,000 µm)	Observation by fluorescence microscope	Polyamide fibers (500 µm) *Goodfellow*	89%

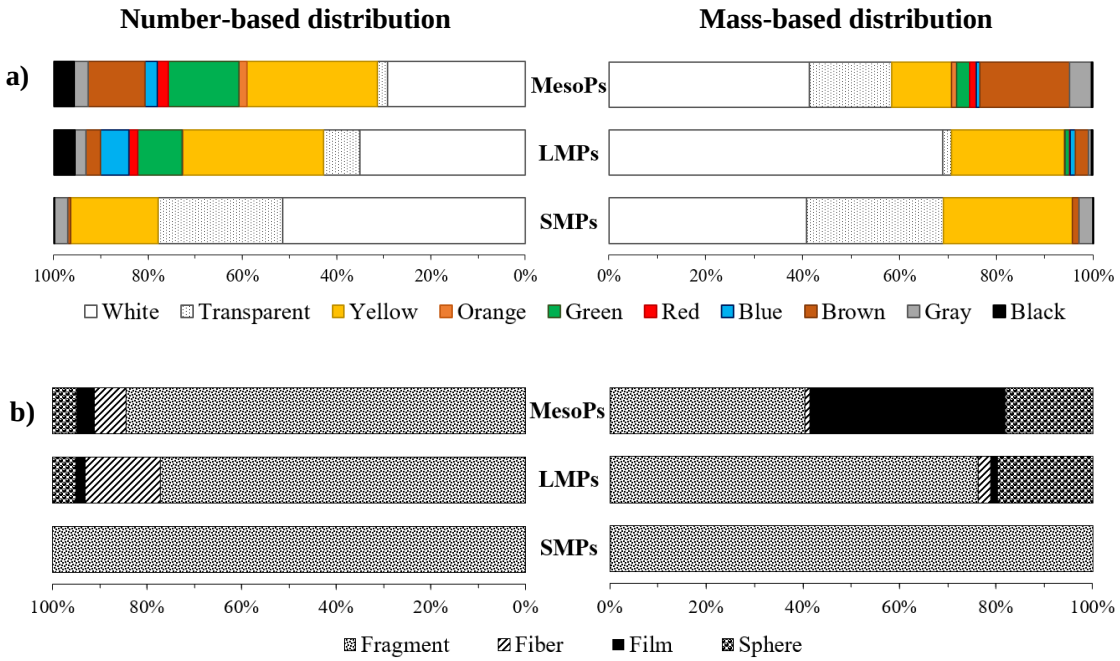


Figure A–1 a) Distribution of the colors of plastics; b) Distribution of the shapes of plastics.

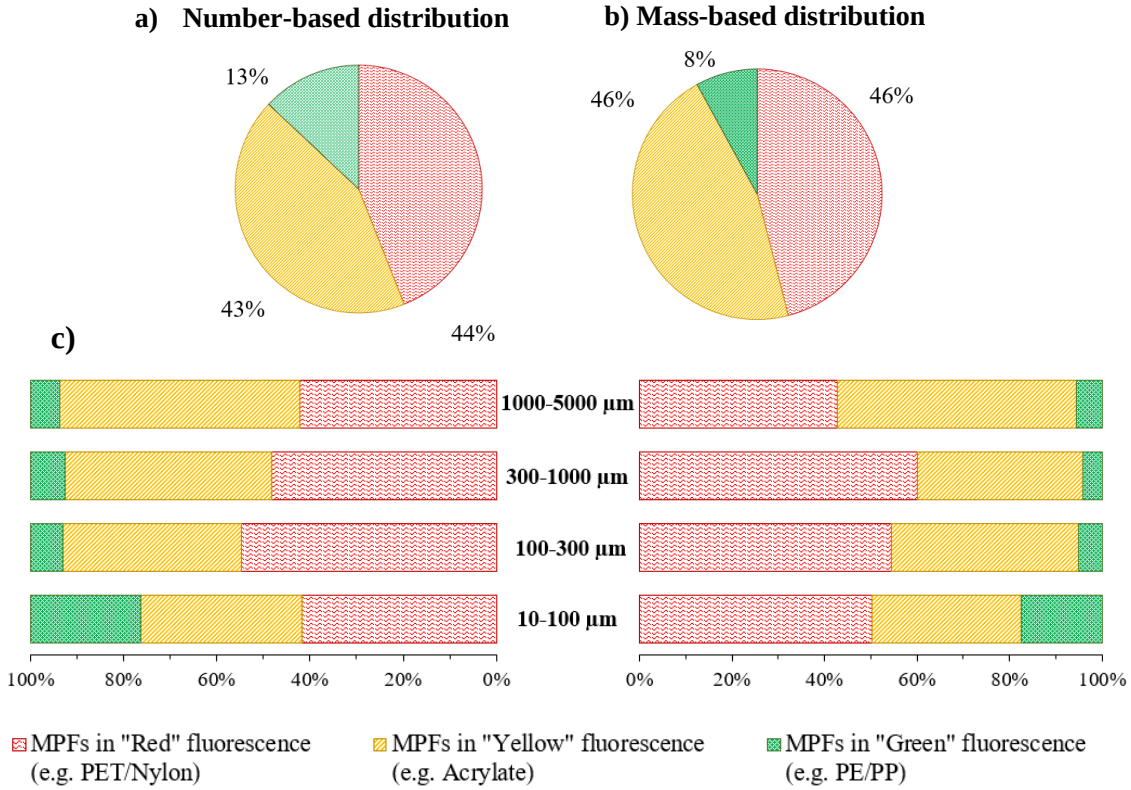


Figure A–2 Distribution of the polymer types of MPFs, a) based on number; b) based on mass; c) based on fiber length ("MPFs" refers to microplastic fibers in the size range of 10–5,000 µm).

Table A–8 Proportions of mesoplastics (out of the total microplastics and mesoplastics) in river

Reference	Study area	Minimum particle size (µm)	Maximum particle size (µm)	Proportion of mesoplastics	
				Number-based	Mass-based
Barrows et al., 2018	River Gallatin, USA	100	9,600	<2%	-
This study	**Rivers of Kyoto City, Japan**	300*	25,000	5%	74%
Baldwin et al., 2016	29 Great Lakes Tributaries, U.S.A	355	>4,750	2%	-
Lenaker et al., 2019	Milwaukee River, USA	355	>4,750	3%	-
Ravit et al., 2017	Raritan and Passaic Rivers, New Jersey, U.S.A	355	>4,750	31%	-
Ding et al., 2019	Wei River, northwest of China	<500	>5,000	<2%	-
Haberstroh et al., 2020	Hillsborough River, U.S.A	500	>5,000	<5%	10-85%
Singh et al., 2021	River Ganga, India	700	7,500	<35%	<60%
Moore et al., 2011	Los Angeles & San Gabriel Rivers, U.S.A	1,000	>4,750	6%	-

**Microplastics between 10–300 µm was omitted from this calculation as the data available for comparison from other studies mostly included microplastics larger than 300 µm.*

Text A–2. Contribution to riverine microplastic emissions by treated wastewater effluent

Daily river discharge at the downstream (Miyamae bridge) = 1,849,000 m^3/day

Daily microplastic loads (10–5,000 µm) at the downstream = 2.9×10^{10} items/day

= 9.0 kg/day

Daily discharge of treated wastewater effluent = 718,000 m^3/day

Daily microplastic loads (10–5,000 µm) discharged through treated wastewater

= 8×10^{9} items/day

= 0.3 kg/day

Volume of treated wastewater discharged into the river per day as a percentage of the daily river flow $= \frac{718{,}000}{1{,}849{,}000} \times 100\% = 38\%$

Microplastic loads in the treated wastewater as a percentage of total microplastic loads discharged through the river network (per day)

Considering number of microplastics $= \frac{8\times10^{9}}{2.9\times10^{10}} \times 100\% = 28\%$

Considering mass of microplastics $= \frac{0.3}{9.0} \times 100\% = 3\%$

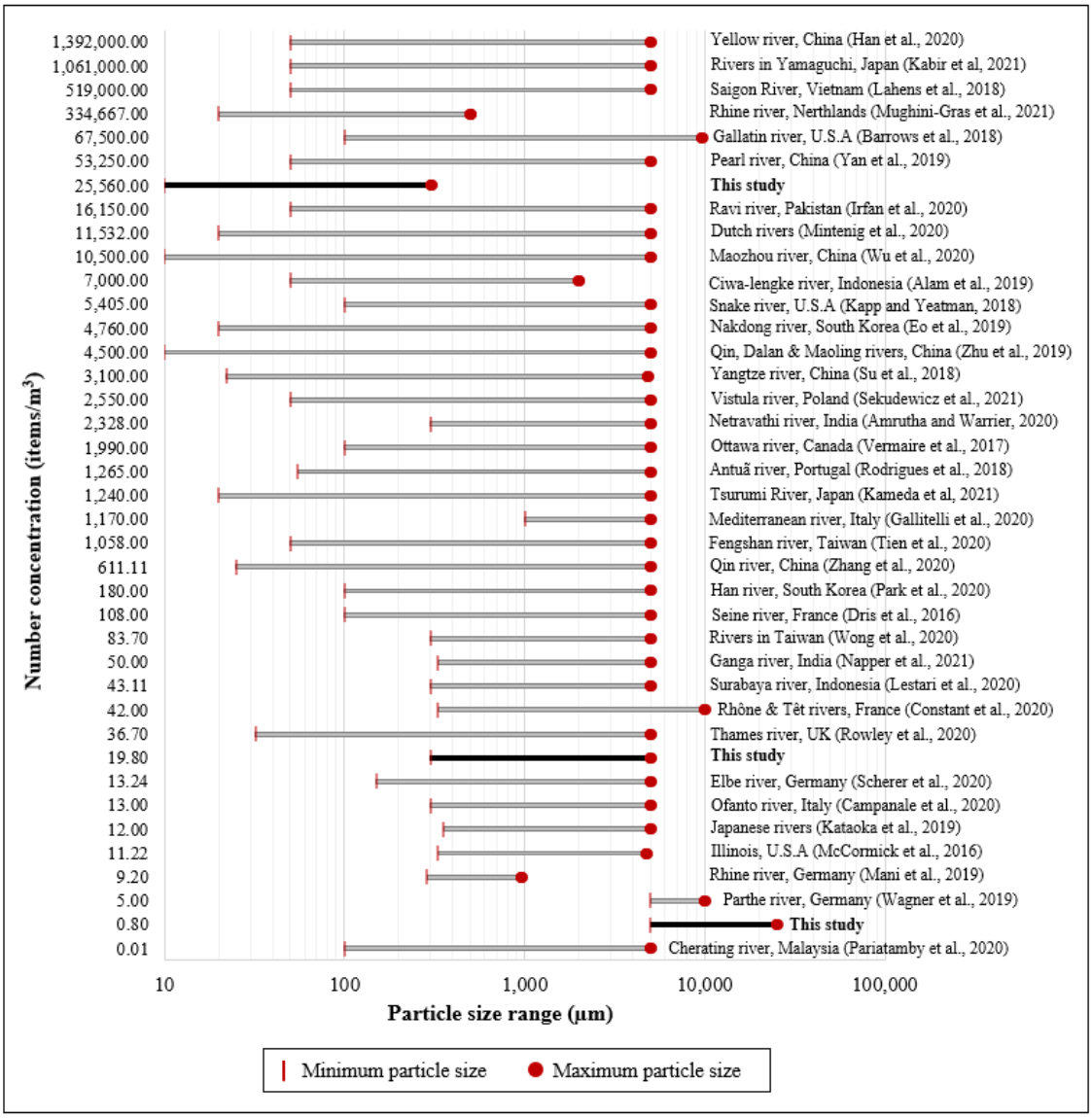
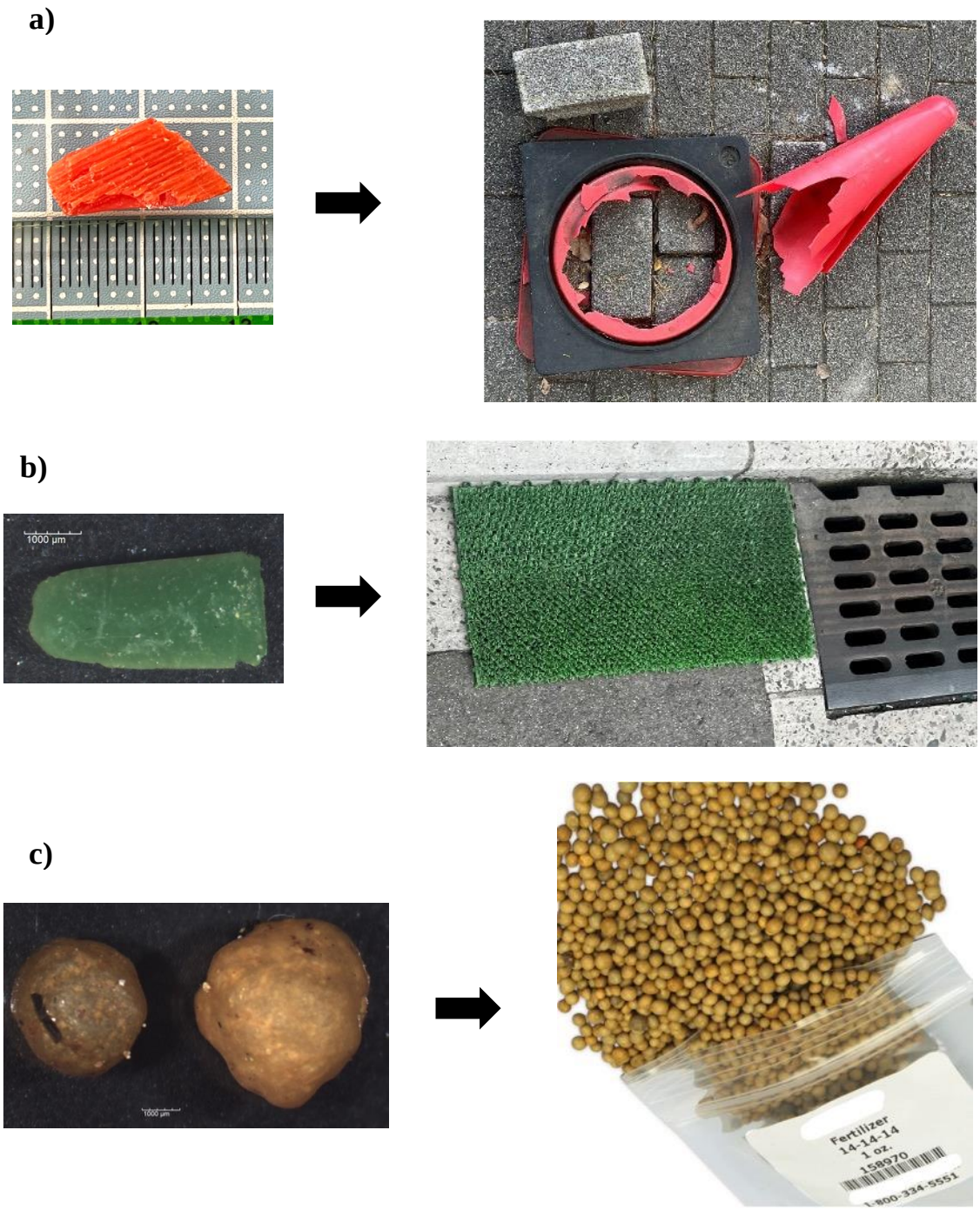


Figure A–3 Comparison of plastic concentrations reported from riverine environments all over the world with the present results



(Source: https://www.carolina.com/wisconsin-fast-plants-supplies/fertilizer-14-14-14-1-oz/158970.pr)

Fig A–4 Plastic particles possibly derived from a) broken road cones, b) artificial grass carpets, and c) fertilizer particles

Appendix B Supplementary Information for Chapter 4

Table B–1 Results of blank tests

Event	Type of sample	Blank test
Event 1	LMPs [a]	0 particles
	SMPs [b]	2 particles
	MPFs [c]	24 fibers
Event 2	LMPs [a]	0 particles
	SMPs [b]	0 particles
	MPFs [c]	22 fibers
Event 3	LMPs [a]	0 particles
	SMPs [b]	4 particles
	MPFs [c]	27 fibers

[a] *Large microplastic particles (300–5,000 µm);* [b] *Small microplastic particles (10–300 µm);* [c] *Microplastic fibers (300–5,000 µm)*

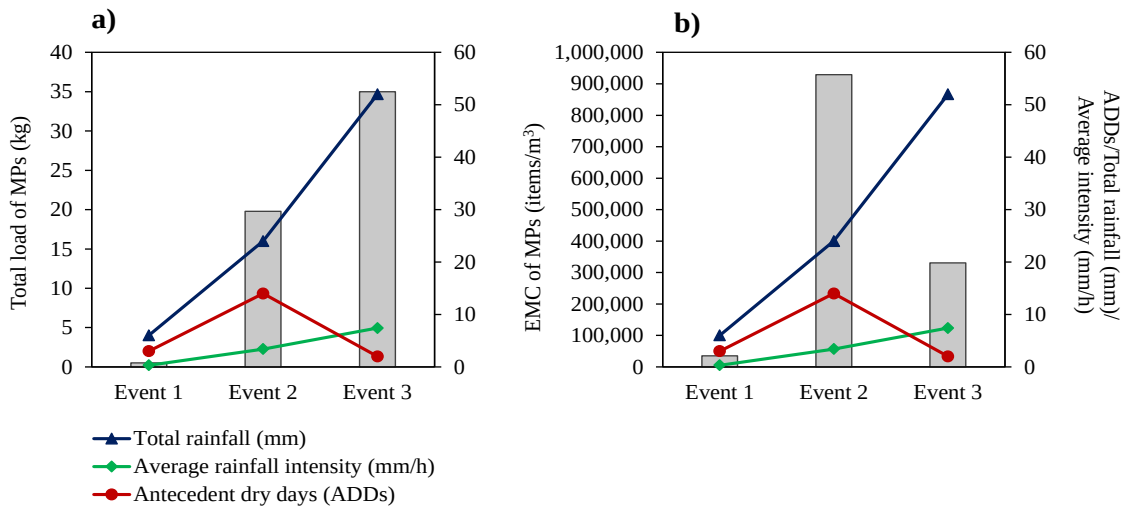


Figure B–1 Relationship between a) total loads of MPs and rainfall characteristics; b) event mean concentrations (EMCs) of MPs and rainfall characteristics ("MPs" refers to microplastic particles)

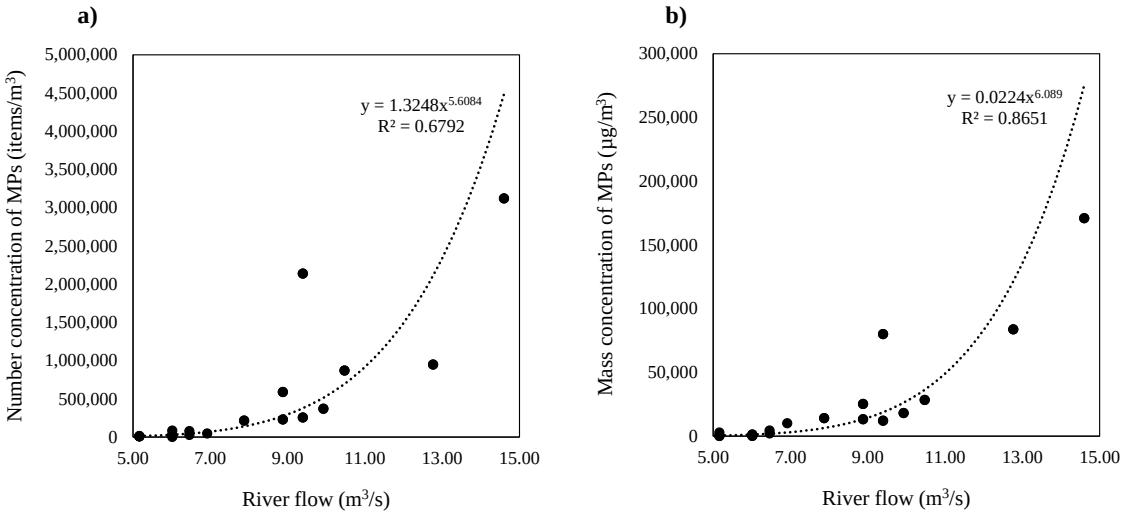


Figure B–2 Relationship between river flow and a) hourly number concentrations of MPs; b) hourly mass concentrations of MPs

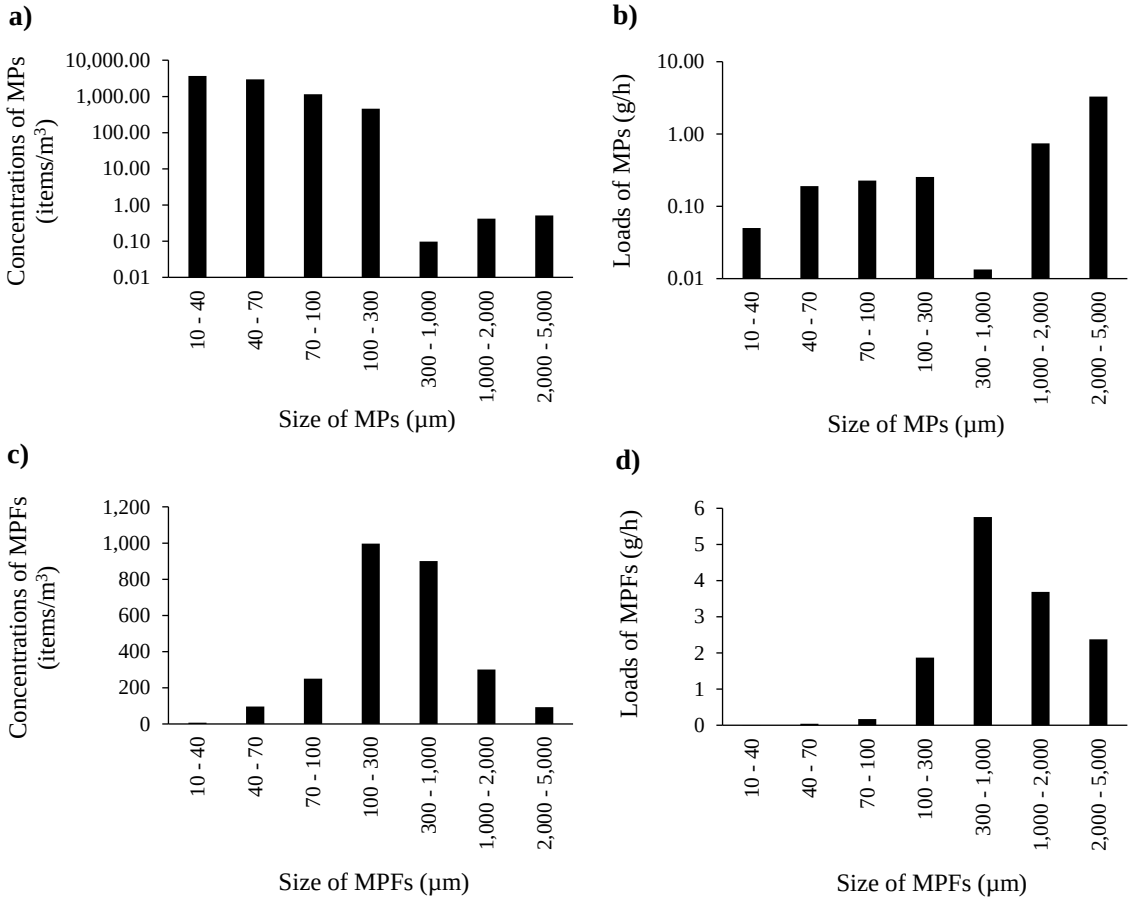


Figure B–3 Size-based distributions of a) Concentrations of MPs, b) loads of MPs; c) concentrations of MPFs; and d) loads of MPFs during dry days ("MPs" refers to microplastic particles; "MPFs" refers to microplastic fibers).

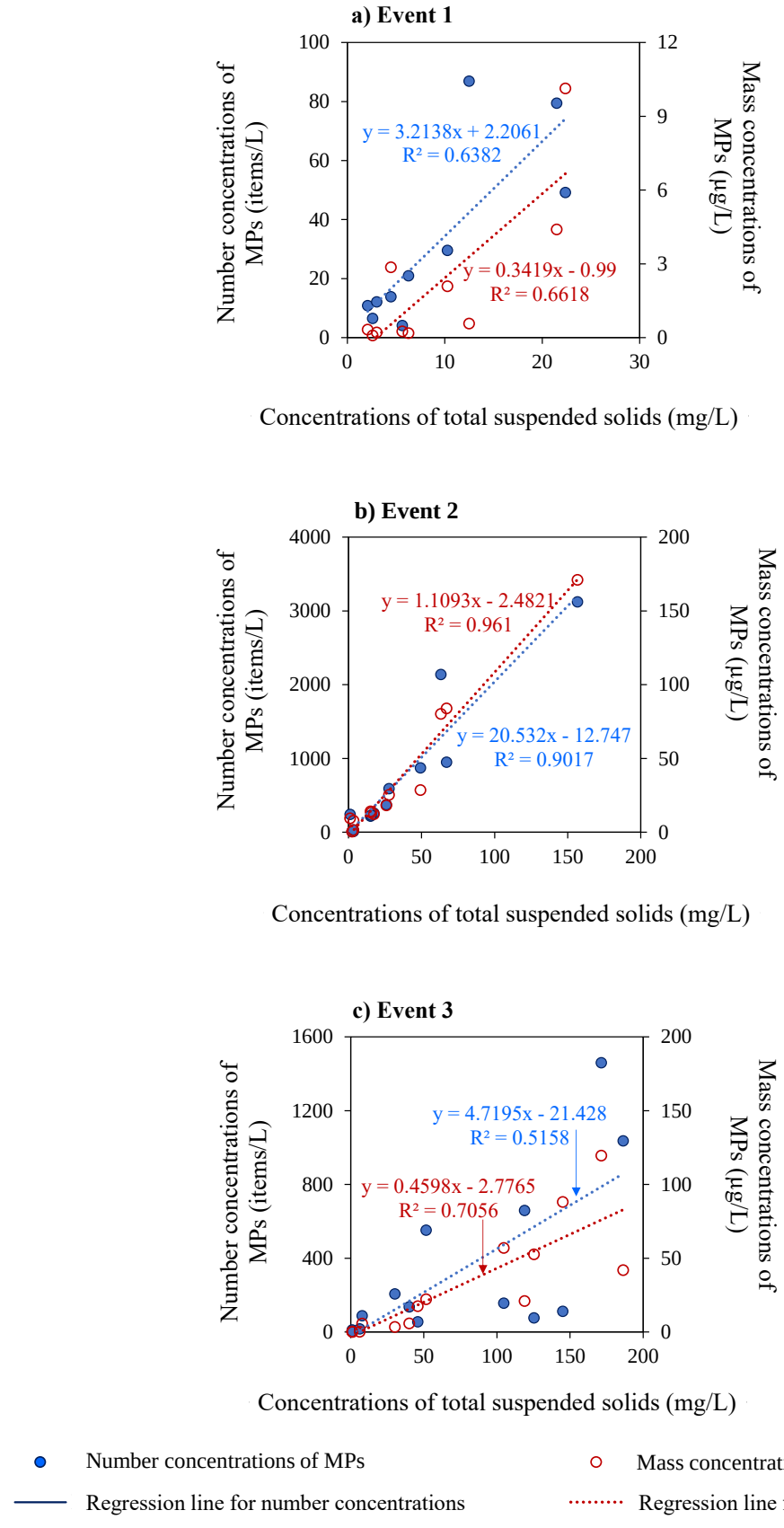


Figure B–4 Relationship between the concentrations of MP particles (MPs) and total suspended solids (TSS) for a) Event 1, b) Event 2 and c) Event 3.

Table B–2 Estimation of the annual loads of microplastic particles (MPs) and fiber (MPFs) in dry and wet days

	Dry days	**Light rain (Event 1)**	**Moderate rain (Event 2)**	**Heavy rain (Event 3)**
No. of days per year (as a percentage of total days per year) [a]	255 (70%)	49 (13%)	39 (11%)	22 (6%)
Loads in terms of number of MPs				
Daily loads of MPs [b] (billion items/day)	3	7	376	348
Annual loads of MPs (billion items/year)	868	335	14,669	7,660
Loads of MPs as a percentage of the total annual load	4%	1%	62%	33%
Loads in terms of mass of MPs				
Daily loads of MPs (kg/day) [b]	0.1	0.5	19.8	35.0
Annual loads of MPs (kg/year)	29	25	771	770
Loads of MPs as a percentage of the total annual load	2%	2%	48%	48%
Loads in terms of number of MPFs				
Daily loads of MPFs [b] (billion items/day)	1.1	1.3	11.5	15.8
Annual loads of MPFs (billion items/year)	277	64	449	349
Loads of MPFs as a percentage of the total annual load	24%	6%	39%	31%
Loads in terms of mass of MPFs				
Daily loads of MPFs (kg/day) [b]	0.3	0.2	1.9	4.0
Annual loads of MPFs (kg/year)	85	10	74	87
Loads of MPFs as a percentage of the total annual load	33%	4%	29%	34%
Annual loads of MPs/MPFs (Number)	3	5	33	22
Annual loads of MPs/MPFs (Mass)	0.3	2	10	9

[a] *No of dry and wet days in the study region were obtained from the website of Japan Meteorological Agency (Data for years 2021 and 2022 were considered). Rainy days were classified as Light, Moderate and Heavy based on the definition explained in Section 2.2 of the manuscript.*

[b] *Daily loads of MPs and MPFs for rainy days were calculated by assuming that a rainfall event may continue throughout a day.*

Appendix C Supplementary Information for Chapter 5

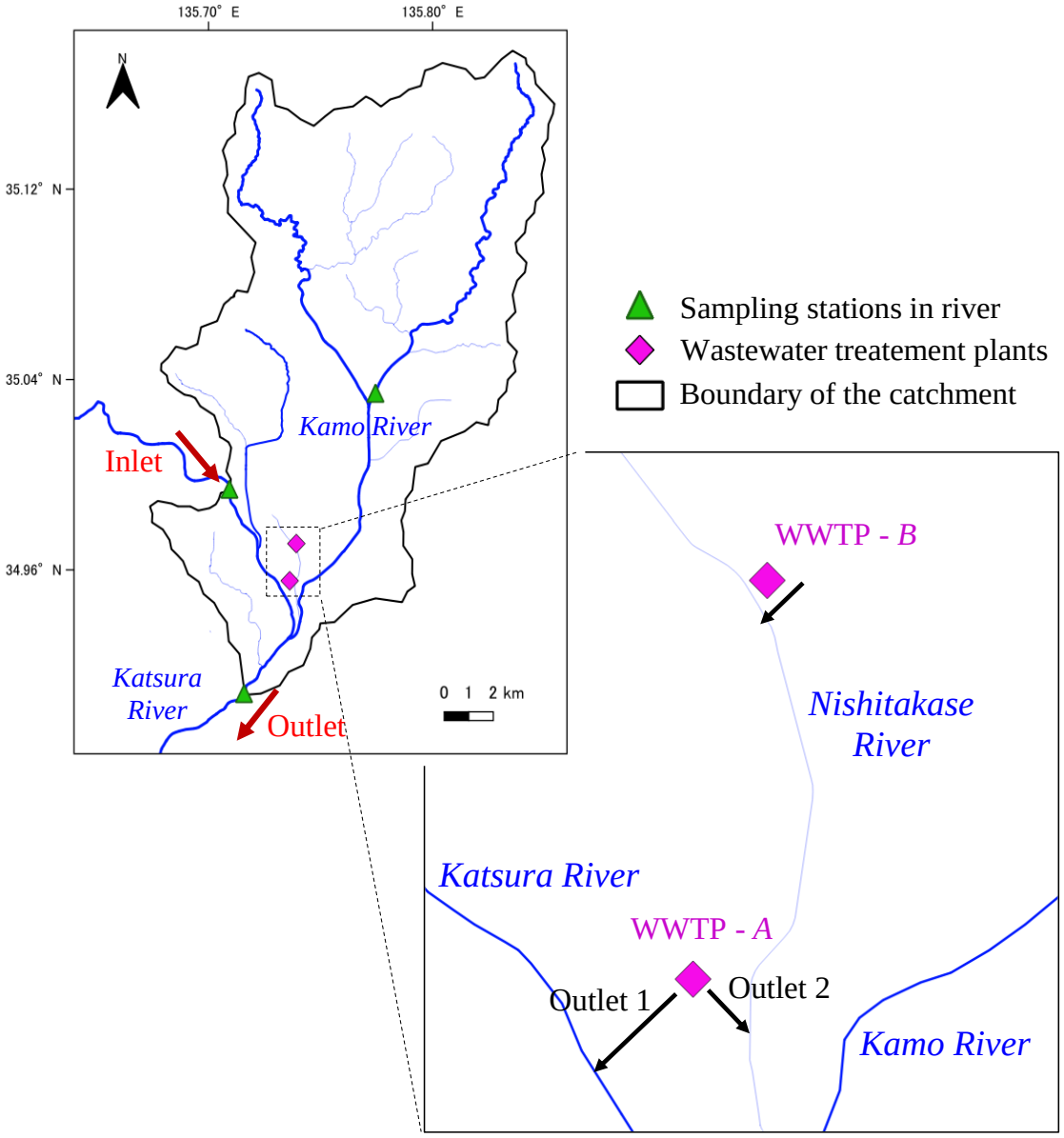


Figure C–1 Treated effluent outlets of the two wastewater treatment plants in the study area

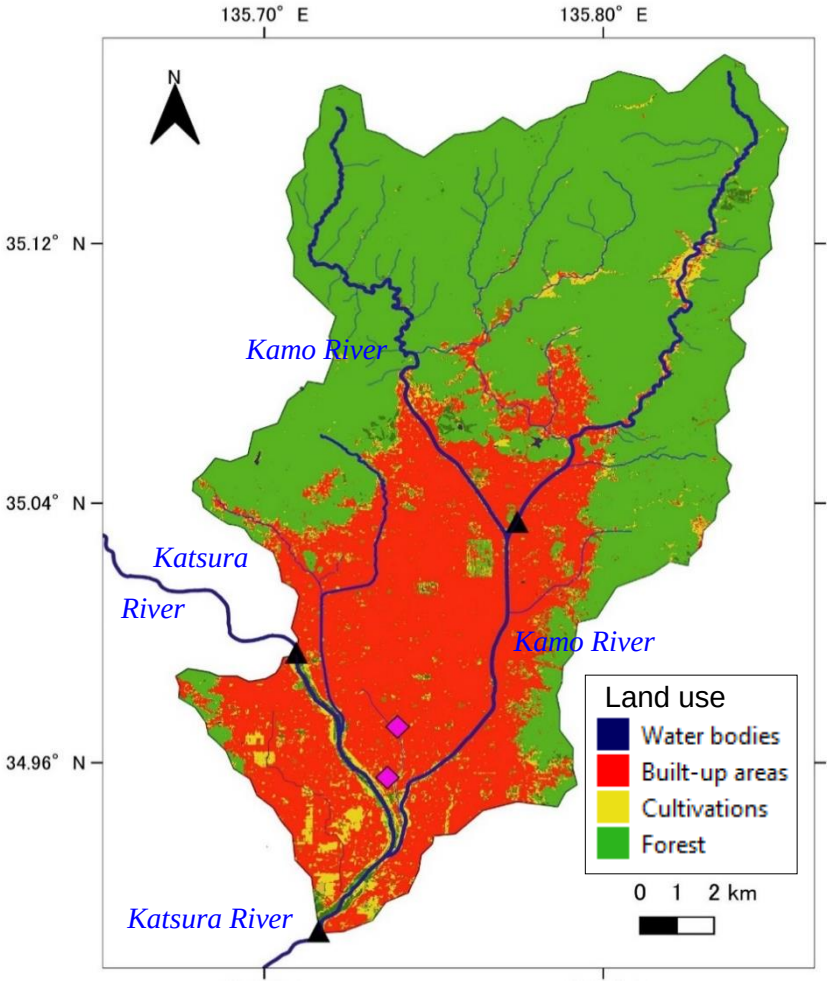


Figure C–2 Land use map of the study area

Table C–1 Results of blank tests

Sampling location and event		Type of sample	Blank test
River – dry weather	Survey 1	300–5,000 µm MPs	0 particles
		10–300 µm MPs	0 particles
	Survey 2	300–5,000 µm MPs	0 particles
		10–300 µm MPs	0 particles
River – wet weather	Light rainfall (Event 1)	300–5,000 µm MPs	0 particles
		10–300 µm MPs	2 particles
	Moderate rainfall (Event 2)	300–5,000 µm MPs	0 particles
		10–300 µm MPs	0 particles
	Heavy rainfall (Event 3)	300–5,000 µm MPs	0 particles
		10–300 µm MPs	4 particles
Wastewater treatment plants		300–5,000 µm MPs	0 particles
		10–300 µm MPs	5 particles

Text C–1. Annual microplastic emissions estimated for varying microplastic concentrations in river water.

The annual microplastic loads discussed in Chapter 5 are calculated based on the average microplastic concentrations in river water during dry weather (these average concentrations were derived from two data sets obtained from sampling river water in August 2021 and October 2021). Here we estimate a range of possible values for annual microplastic loads, considering 27 cases derived from different combinations of data sets as shown in Table C–2 and Table C–3.

Table C–2 Microplastic concentrations in river water expressed in µg/m^3

	Nishioh bridge (catchment inlet)	Miyamae bridge (catchment outlet)	Mikage bridge
C_{Aug}	598	6,492	208
C_{Oct}	390	2,505	350
C_{Mean}	484	5,024	279

C_{Aug}: Microplastic concentrations in river water in August 2021 (dry weather)
C_{Oct}: Microplastic concentrations in river water in October 2021 (dry weather)
C_{Mean}: Average microplastic concentrations in river water during dry weather (combined data from August and October 2021)

Table C–3 Definition of the 27 cases considered in estimating annual microplastic emissions

	Nishioh bridge [a]	Miyamae bridge [b]	Mikage bridge [c]		Nishioh bridge [a]	Miyamae bridge [b]	Mikage bridge [c]
Case 1	C_{Aug}	C_{Aug}	C_{Aug}	Case 14	C_{Oct}	C_{Aug}	C_{Mean}
Case 2	C_{Aug}	C_{Aug}	C_{Oct}	Case 15	C_{Oct}	C_{Oct}	C_{Mean}
Case 3	C_{Aug}	C_{Oct}	C_{Aug}	Case 16	C_{Oct}	C_{Mean}	C_{Aug}
Case 4	C_{Aug}	C_{Oct}	C_{Oct}	Case 17	C_{Oct}	C_{Mean}	C_{Oct}
Case 5	C_{Aug}	C_{Aug}	C_{Mean}	Case 18	C_{Oct}	C_{Mean}	C_{Mean}
Case 6	C_{Aug}	C_{Oct}	C_{Mean}	Case 19	C_{Mean}	C_{Aug}	C_{Aug}
Case 7	C_{Aug}	C_{Mean}	C_{Aug}	Case 20	C_{Mean}	C_{Aug}	C_{Oct}
Case 8	C_{Aug}	C_{Mean}	C_{Oct}	Case 21	C_{Mean}	C_{Aug}	C_{Mean}
Case 9	C_{Aug}	C_{Mean}	C_{Mean}	Case 22	C_{Mean}	C_{Oct}	C_{Aug}
Case 10	C_{Oct}	C_{Aug}	C_{Aug}	Case 23	C_{Mean}	C_{Oct}	C_{Oct}
Case 11	C_{Oct}	C_{Aug}	C_{Oct}	Case 24	C_{Mean}	C_{Oct}	C_{Mean}
Case 12	C_{Oct}	C_{Oct}	C_{Aug}	Case 25	C_{Mean}	C_{Mean}	C_{Aug}
Case 13	C_{Oct}	C_{Oct}	C_{Oct}	Case 26	C_{Mean}	C_{Mean}	C_{Oct}
				Case 27	C_{Mean}	C_{Mean}	C_{Mean}

[a] *This data is used to calculate microplastic loads at the catchment inlet*
[b] *This data is used to calculate microplastic loads at the catchment outlet*
[c] *This data is used to estimate the factors by which the microplastic loads in river water increases during rainfall events with respect to the loads during dry weather.*

Table C–4 Annual emissions considering 27 different cases

			Values based on average data (Case 27)	Minimum value from all cases	Maximum value from all cases
Dry weather - MP emissions	UCE_{dry}	kg	2,134	922	2,849
	CE_{in}	kg	39,440	39,440	39,440
	CE_{out}	kg	72	72	72
	Annual MP emissions (without WWTP treatment)	kg	41,574	40,362	42,289
	Annual MP emissions (with WWTP treatment)	kg	2,206	993	2,921
	% of UCE_{dry} without WWTP treatment		5.1%	2.3%	6.7%
	% of CE_{in} without WWTP treatment		94.9%	93.3%	97.7%
	% of UCE_{dry} with WWTP treatment		96.8%	92.8%	97.6%
	% of CE_{out} with WWTP treatment		3.2%	2.4%	7.2%
Wet weather - MP emissions	UCE_{wet}	kg	210,119	31,360	275,770
	CE_{in}	kg	17,460	17,460	17,460
	CE_{out}	kg	32	32	32
	Annual MP emissions (without WWTP treatment)	kg	227,578	48,819	293,230
	Annual MP emissions (with WWTP treatment)	kg	210,150	31,391	275,802
	% of UCE_{wet} without WWTP treatment		92.3%	64.2%	94.0%
	% of CE_{in} without WWTP treatment		7.7%	6.0%	35.8%
	% of UCE_{wet} with WWTP treatment		100.0%	99.9%	100.0%
	% of CE_{out} with WWTP treatment		0.0%	0.0%	0.1%
Annual MP emissions	UCE_{dry}	kg	2,134	922	2,849
	UCE_{wet}	kg	210,119	31,360	275,770
	CE_{in}	kg	56,900	56,900	56,900
	CE_{out}	kg	103	103	103
	Annual MP emissions (without WWTP treatment)	kg	269,153	89,182	335,519
	Annual MP emissions (with WWTP treatment)	kg	212,356	32,385	278,723
	% of UCE_{dry} without WWTP treatment		0.8%	0.6%	1.9%
	% of UCE_{wet} without WWTP treatment		78.1%	35.2%	82.2%
	% of CE_{in} without WWTP treatment		21.1%	17.0%	63.8%
	% of UCE_{dry} with WWTP treatment		1.0%	1.0%	3.0%
	% of UCE_{wet} with WWTP treatment		98.9%	96.8%	98.9%
	% of CE_{out} with WWTP treatment		0.0%	0.0%	0.3%

Microplastic emissions in the form of CE and UCE are calculated for each case (Table C–4) following the calculation methods exemplified in Table 5–6 for Case 27 (this case considers the average microplastic concentrations at each river station). Table C–4 presents only the minimum and maximum values derived out of all 27 Cases. The range of possible emissions values are expressed as "**minimum value from all cases"** – "**maximum value from all cases"**.

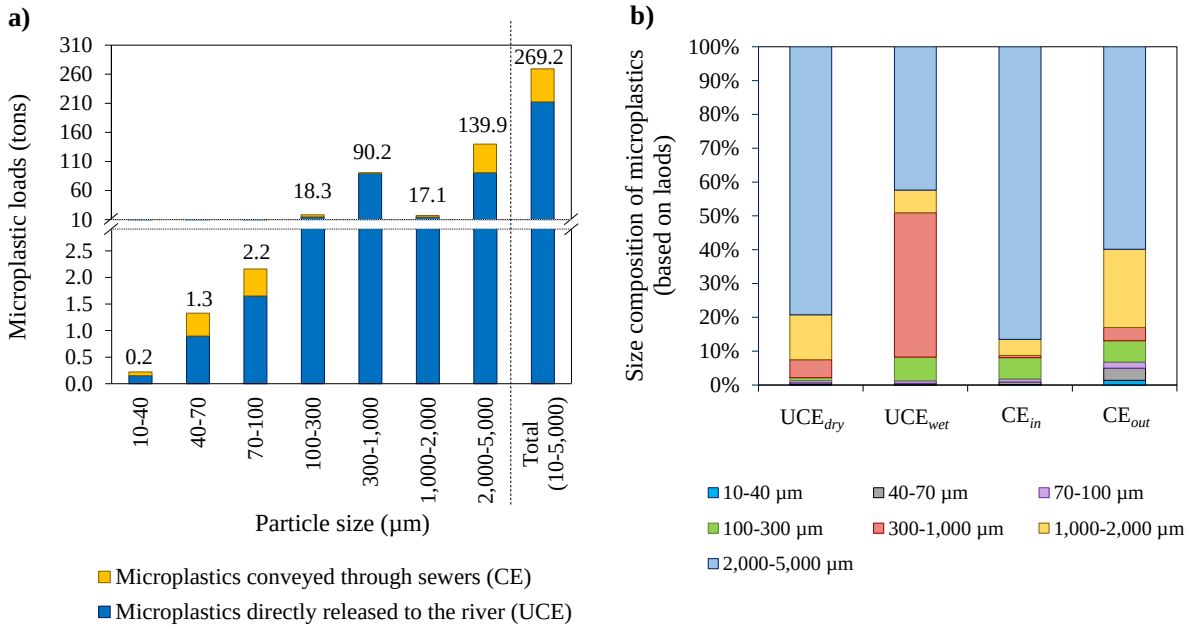


Figure C–3 a) Total microplastic stocks of the catchment including the fractions being treated by wastewater treatment plants (WWTPs) and freely released to the receiving waters; and b) Size composition of microplastics (based on the loads) in uncontrolled emissions and controlled emissions (UCE_{dry} refer to uncontrolled emissions of microplastics in dry weather; UCE_{wet} refers to uncontrolled emissions of microplastics in wet weather; CE_{in} refers to controlled emissions of microplastics through WWTP influent; and CE_{out} refers to controlled emissions of microplastics through WWTP effluent).

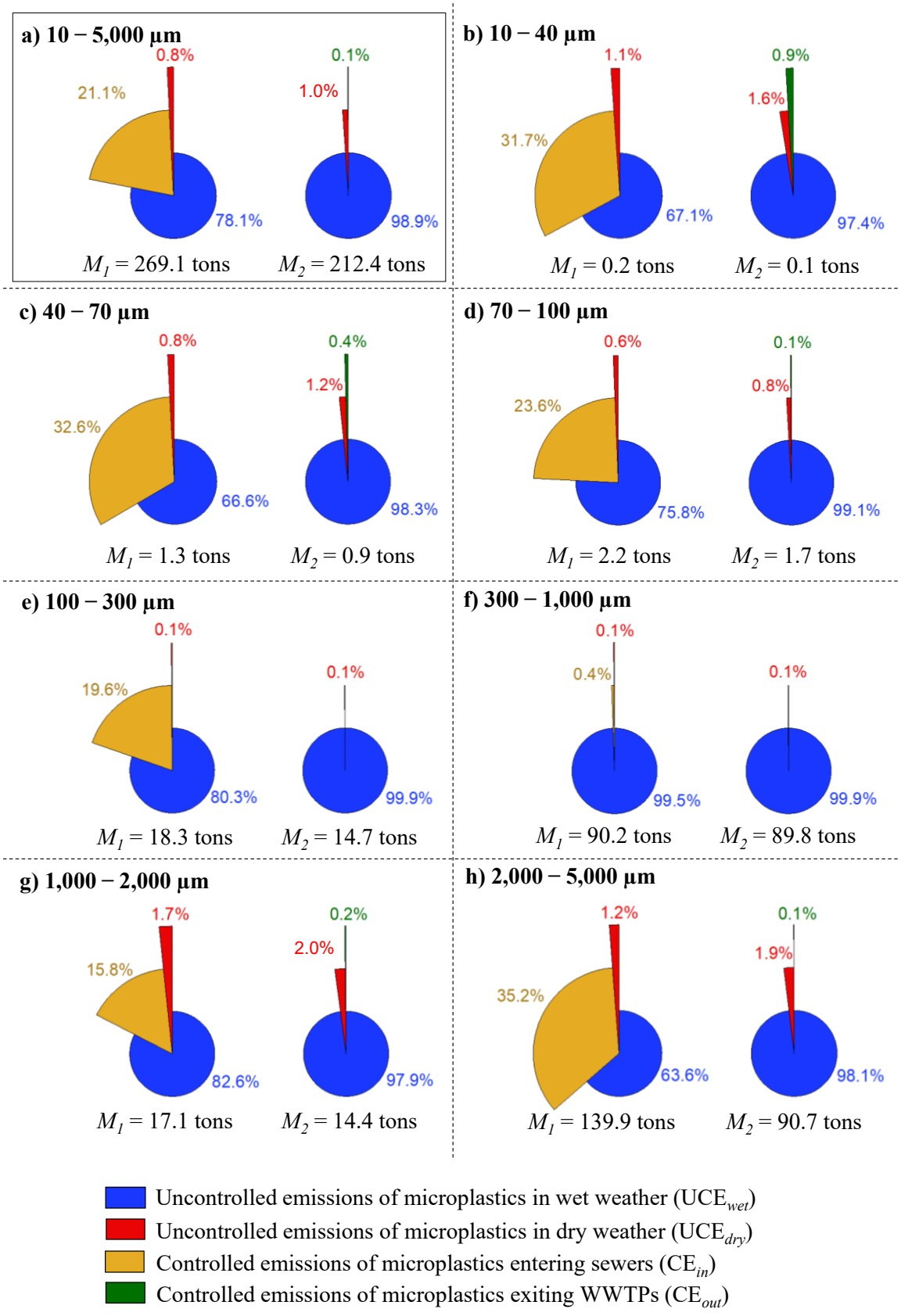


Figure C–4 Total microplastic emissions of the catchment (expressed in tons) for different size clusters (M_1 indicates the total emissions without considering treatment whereas M_2 indicates the total emissions considering treatment).