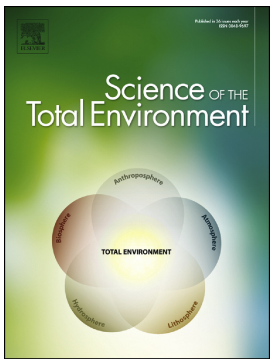

Microplastics in the sediments of small-scale Japanese rivers: Abundance and distribution, characterization, sources-to-sink, and ecological risks

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Microplastics in the Sediments of Small-scale Japanese Rivers: Abundance and Distribution, Characterization, Sources-to-sink, and Ecological Risks

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Abstract

Microplastic pollution in small-scale river sediments remains mostly unknown. This study explored microplastics in the sediments of four small-scale Japanese rivers in Yamaguchi Prefecture: the Awano, Ayaragi, Asa, and Majime. Sediment samples (n=23) were collected from the selected stations. Density separation and wet peroxidation methods were applied to extract microplastics. Polymers were detected through attenuated total reflectance-Fourier transform infrared spectroscopy. Microplastic abundance indicated relatively moderate values in the small-scale Japanese rivers compared to other rivers around the world. Large microplastics (1–5 mm) in size, fragments in shape, and high-density particles of diverse polymers dominated. Polyvinyl chloride, polyethylene, and polypropylene were the major polymers. The polymers— polyvinyl chloride, polymethylmethacrylate, polyurethane, fluorinated ethylene propylene, and polybutylene in sediments were distinct from those detected in surface water, as were the predominance of large-size (1–5 mm) and fragment-shape microplastics. In contrast to surface water, sediments preserved both common and distinctive microplastics. Thus, the riverine sediment compartment acted as microplastic sink. Scanning electron microscopic (SEM) analysis suggested the presence of weathered microplastics in sediments. Energy dispersive X-ray spectroscopic analysis (EDX) revealed metal contaminants on the microplastic surfaces, indicating synergistic hazard potentials in the riverine ecosystems. Ecological risk assessment results suggested low to very high risks of microplastic pollution for the rivers. The higher abundances of microplastics and highly toxic polymers contributed to the elevated ecological risks. Polyvinyl chloride, acrylonitrile butadiene styrene, polyurethane, and polymethylmethacrylate were the detected highly toxic polymers. The urban and residential areas affected stations ranked high to very high ecological risks. The sites posing very high ecological risks were regarded as pollution hotspots. Overall, this study developed

new insights into microplastic pollution in the small-scale rivers and ecological risks for riverine environments, as well as providing a baseline for more comprehensive risk assessments and developing pollution control and management strategies.

Key Words: Small-scale Rivers, Sediment, Microplastics, Ecological Risks, Sink.

1. Introduction

Plastic pollution has become a growing threat to planetary health (Villarrubia-Gómez et al., 2018). The tiny plastic particles (<5 mm) which are regarded as Microplastics (MPs), and a type of plastic pollutants (Arthur et al., 2009). MPs are ubiquitous in all terrestrial and aquatic (freshwater and marine) environmental components such as water, biota, soil, and sediments across the planet (Auta et al., 2017; Büks and Kaupenjohann et al., 2020; Li et al., 2018; O'Connor et al., 2019; Van Cauwenberghe et al., 2015). MP pollutants possess diverse characteristics (shapes-sizes-colors-polymers), are toxic and pervasive; they pose ecotoxicological threats across the global environments (Andrady, 2011; Cole et al., 2011; Peng et al., 2020; Rochman et al., 2019; Wright et al., 2013).

Globally rivers are MP pollution hotspots and counter numerous ecological threats (Eerkes-Medrano et al., 2015; Schmidt et al., 2017; Simon-Sánchez et al., 2019; van Emmerik and Schwarz, 2020). Rivers provide highly dynamic environments for MP pollutants functioning as the initial sink of MPs as well as the major conduits for emitting MPs into the ultimate sink, that is, the marine realm (Cheung et al., 2018; Schmidt et al., 2017; Simon-Sánchez et al., 2019). However, in riverine ecosystems, little is known regarding environmental behaviors of MPs and the pollution (Bletter et

al., 2018; Horton et al., 2017). Although flowing waters continuously discharge river MPs to the sea, riverbed sediments are prone to retain MPs. In fact, there is an increasing abundance of MPs in river sediments, referred to as MP accumulation hotspots (Klein et al., 2015; Mani et al., 2019; Nizzetto et al., 2016a; Simon-Sánchez et al., 2019). In addition, environmental behavior of MPs differs between sediments and water (Scherer et al., 2020). There exists a knowledge gap regarding the MPs retained in sediments, and their types and characteristics. Furthermore, small-scale freshwater bodies were found to be highly polluted with MPs (Hu et al., 2018; Kabir et al. 2021; Luo et al., 2019). Kabir et al. (2021) reported that small-scale Japanese rivers were highly polluted as compared to the large rivers around the world. They were also the prominent conduits responsible for causing marine MP pollution. Thus, small-scale rivers are one of the most important freshwater ecosystems that are vulnerable to MP pollution. However, knowledge regarding the MPs in the small-scale riverine sediments remains insignificant.

The primary source of MPs includes the industrial products (e.g., personal care products, fertilizers for agriculture, household and industrial items such as detergents, cleaning products, paints, etc.). Secondary MPs result from the breakdown of larger plastic particles under various environmental conditions (photo-oxidation, weathering, biodegradation, and mechanical abrasion etc.) (Cole et al, 2011; Lambert and Wagner, 2018; Scudo et al., 2017). Land sources are the major contributors of (micro-)plastics to aquatic systems (Boucher et al., 2017; Jambeck et al., 2015). Both point (i.e., population density, urban, domestic sewage, and wastewater treatment plants [WWTPs], industries, etc.) and non-point (forest, agricultural, atmospheric fallouts, airborne, etc.) sources generate and emit MPs (Allen et al., 2019; Baldwin et al., 2016; Dris et al., 2018; Kataoka et al., 2019; Murphy et al., 2016; Siegfried et al., 2017). However, there is a lack of information regarding the influences of point and non-point land-use sources on MP emissions in sediments at

river catchment scales. Moreover, land-use sources at river catchment scales may suggest the location regarding preferential buildup of MP accumulation hotspots in riverine environments. Therefore, this type of knowledge is highly imperative for the development of practical approaches in relation to pollution control and management.

With diverse characteristics (shape-size-color-polymers), MPs are hazardous as diverse pollutant suites (Rochman et al., 2019). MPs act as vectors of organic pollutants, metal contaminants, and microbial pathogens (Wang et al., 2020; Yu et al., 2019; Zhang et al., 2020). As a result, MP contaminants in aquatic environments have the potential to cause synergistic hazards and increase toxicity. Besides, once MPs are incorporated into environmental matrices, they undergo weathering processes (Liu et al., 2020). It is evident that weathered MPs adsorb and desorb other toxic contaminants, as well as leach the plastic containing toxic chemicals increasingly (Liu et a. 2020; Sun et al. 2020). There are, however, gaps in understanding of whether MPs in river sediments are weathered and vectorize other pollutants. As riverine water-sediment interfaces are highly crucial ecological components for providing food sources and habitats for aquatic species (ASCE Task Committee on Sediment Transport and Aquatic Habitats, Sedimentation Committee, 1992; Shumchenia et al., 2016), MPs and their associated contaminants in riverine sediments pose increasing threats likely — habitat degradation, contaminate the food web, and encounter MP ingestion by biota uptake, ingestion, and contact (de Sá et al., 2018; Eerkes-Medrano et al., 2015; Mani et al., 2019).

Plastics are composed of diverse polymers. All the polymers are not equally toxic; rather, they are classified as low to high toxic in varying degrees (Lithner et al., 2011). Thus, MPs pose risks to ecosystems with a set of diverse polymers. Until recently, the risks of MPs to the

ecosystems remain contrary to being understood (Galloway, 2015; Koelmans et al., 2017). Kabir et al. (2021) developed an MP pollution risk assessment formula and empirically determined that high pollution risks are linked to higher abundances and the presence of toxic polymer types. Despite the widely reported MP abundances, the knowledge of ecological risks remains unknown, particularly for riverine sediment environments at catchment scales. Understanding ecological risk is significant for obtaining insights into MP pollution, threats, and impacts, along with its application in policy-making approaches. What's more, MP pollution risk knowledge is a prerequisite for understanding human-biophysical entities (e.g., biocoenoses, ecosystems) and socio-ecological dimensions towards the sources and generation of risk by human societies, strengthening scientific risk evaluation of microplastics, social responses, and problems of risk reduction and management (Kramm and Völker, 2018).

Japan, one of the world's mega economies, has a long history of invention, industrial development, and the use and application of plastics. MP pollution is regarded as an influential problem of paramount importance for the country (Isobe et al., 2015). To date, Japanese riverine MP pollution is not well understood. In particular, MP pollution in the Japanese river sediments remains unknown. Kabir et al. (2021) was the first study regarding MP pollution the small-scale Japanese rivers, assessing the pollution risks, and estimating MP emission into Japanese Seto Inland Sea (SIS) and Sea of Japan (SJ) by the rivers. However, MPs in small-scale riverine sediments are indispensable to comprehensively understand terrestrial source-to-sinks and riverine MP pollution. This study is the first to investigate MPs in the sediments of small-scale Japanese rivers, identify the potential land-use sources affecting MP occurrences, understand the source-to-sinks phenomena, assess the ecological risks, and identify the hotspots. Therefore, this study will contribute to a

comprehensive understanding of riverine MP pollution and ecological toxicity, address the knowledge gaps, and develop practical measures for control, management, and risk reduction.

2. MATERIALS AND METHODS

2.1. Study Areas and Sample Collection

Four Japanese rivers— Awano (AR), Ayaragi (AyR), Asa (AsR), and Majime (MR) were selected from the Yamaguchi Prefecture of Japan to investigate MPs in sediments (Fig. 1). All the rivers were small-scale by lengths and catchment areas. The length and catchment areas are as follows: AR (74.7 km and 185.9 km^2), AyR (18.6 km and 37.9 km^2), AsR (44 km and 232 km^2), and MR (10.2 km and 18.8 km^2). The AR and AyR flow into the SJ, and the AsR and MR flow into the SIS, respectively. The land-use information (e.g., urban and residential, agricultural, forests, WWTP and other areas) along the river catchments were used for selecting sampling points. The river basin land-use vector data for every square of a 100 m-mesh were obtained from the National Land Numerical Information (NLNI) services of Japan. 'e-Stat, Statistics of Japan' provided the population vector data for each square of a 250 m-mesh. The land-use and population information were calculated using ArcGIS v.10.6.1 (Esri, USA).

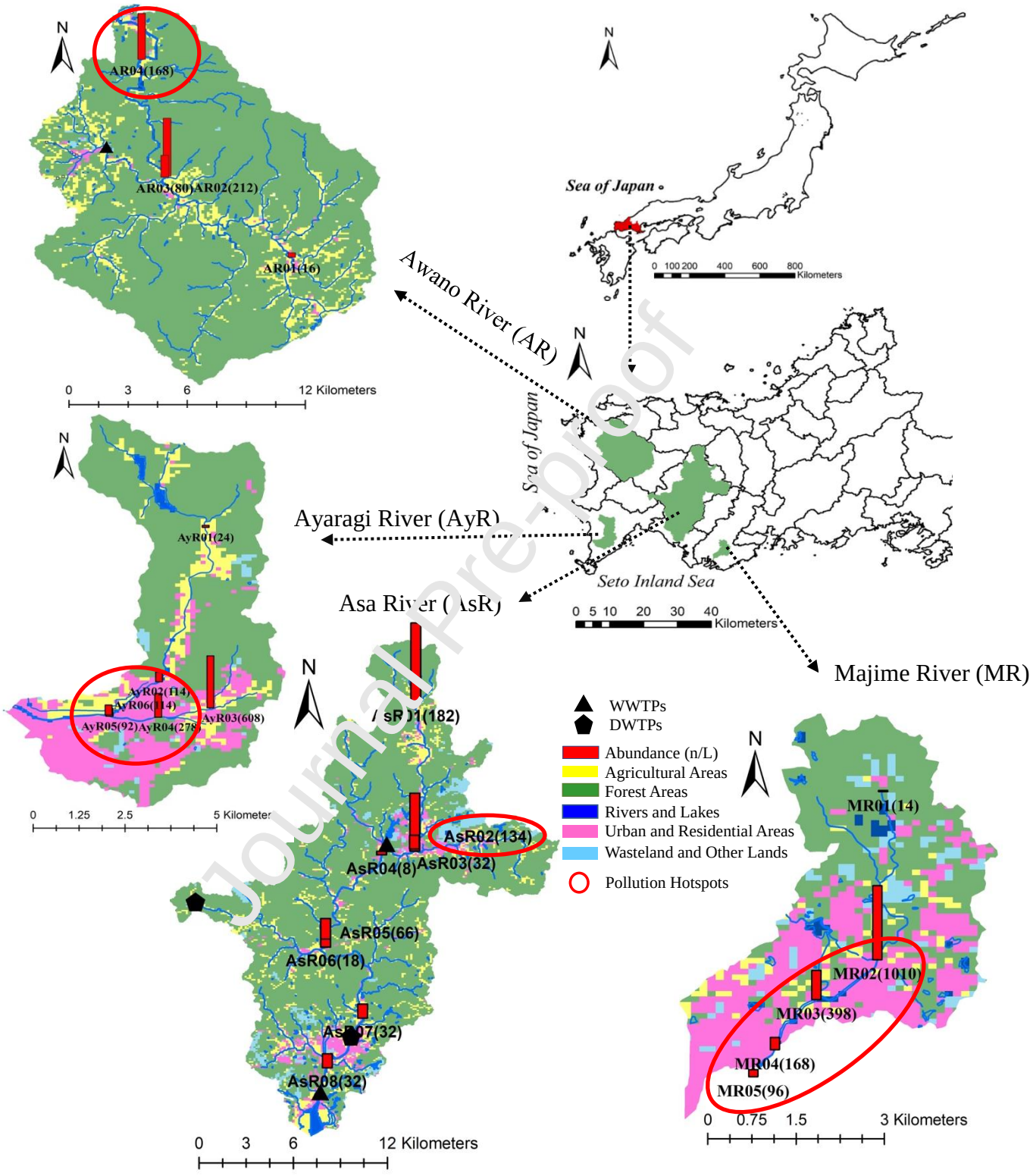


Fig. 1. Catchment land-use pattern, microplastic abundances, and risk levels along the Awano and Ayaragi (Sea of Japan-flowing) and Asa and Majime (Seto Inland Sea-flowing) rivers in

Yamaguchi Prefecture, Japan. Red bars represent the MP abundances (n/kg). Red circles indicate MP pollution hotspots.

The sampling stations were selected along the (up-, mid-, and down-) stream reaches of the rivers based on the catchment land-use patterns over point and non-point sources. The upstream stations (AR01 from AR, AyR01 from AyR, AsR01 and AsR03 from AsR, and MR01 from MR) were less human populated and occupied mostly by non-point sources such as forest and agricultural areas. Both the point (urban and residential areas, populations, and WWTPs) and non-point (agricultural and forest) sources dominated the midstream stations (AR02 and AR03 of the AR, AyR03 of the AyR, AsR04-AsR06 of the AsR, MR02 of the MR). The downstream stations (AR04, AyR02 and AyR04-AyR06, AsR07-AsR08, and MR03-MR05) were mostly influenced by point sources (urban and residential areas; higher number of populations than the up- and mid-stream areas), except for AR04, which was dominated by agriculture and forest areas (Fig. 1). The supplementary information (Table S1) contains details regarding the river basin areas and their land uses.

The standardized protocol for monitoring microplastics in sediments' guidelines by Frias et al. (2018) was followed for sampling of river sediments with adjustments. In brief, approx. 1 kg (dry weight) river sediment was collected maintaining approx. 5 cm depth from the sediment surface per sampling from the selected 23 stations. At some points, the 5 cm depth couldn't be maintained exactly as the sediment layers were not found at that depth. Japanese rivers are of short lengths and steep gradient: flow rapidly and violently due to the narrow and mountainous topography of the country, and the large volume of sediment get runoff (https://www.mlit.go.jp/river/basic_info/english/land.html). Due to river this geomorphological and hydrological facts, some points were not found containing sediment at that projected depth. At those

points, we took the samples at the depths as much as we could. We used metallic shovel to collect sediment samples. The blade of the shovel was rectangular with the length of 0.3 m and width of 0.25 m. Thus, we took the samples using shovel and sampling areas were around 0.3 x 0.25 m^2, and the area volume was approx. 0.3 × 0.25 × 5 m^3 per sample point. An aluminum foil bag was used to cover and store the samples immediately after collecting the samples from each sampling site. Further, the samples were stored in boxes and taken to the laboratory for analysis. The sampling tools and instruments implemented were cleaned and prepared in advance. The AR and AsR river samples were collected on September 9, 2019 while the samples from the AyR and MR rivers were collected on September 10, 2019.

2.2. Sample Preparation and Laboratory Analysis

We followed the protocol demonstrated in Masura et al. (2015) and Rodrigues et al. (2018) with adjustments for the analysis of MP particles in river sediment samples. MP particles were isolated from the samples using density separation and wet peroxidation (WPO) techniques.

In the first step, the sediment samples were entirely placed in an oven, kept at 90 °C for 24 h, and dried. After drying, the samples were sieved, and materials larger than 5 mm in size were removed. Further, 500 g of dry sediment from each sample was placed into the prepared beakers for density separation. Then, 500 mL of the prepared zinc chloride ($ZnCl_2$) solution with a density of 1.5 g/cm^3 was poured into each of the sediment samples containing beakers (Coppock et al., 2017). Each of the sediment-solution mixtures in the beakers was stirred vigorously for at least 15 min. They were further allowed to settle for 24 h for each sample. After that, the resulting supernatants were sieved through a stainless-steel sieve of 0.05 mm. Thus, all floating objects varying in sizes from 0.05 mm to 5 mm were separated. The sieves were rinsed well to ensure that all particles were

transferred to beakers. To ensure that the particles were well extracted, the entire procedure was repeated at least three times for each sample. All extracted particles from each sample were collected in beakers. After extraction, the beakers were immediately covered with aluminum foil, placed in an oven, and dried at 80 °C. After drying, the beakers containing extracted particles were placed in a fume hood (DALTON, DF-11AK) to proceed to the second step.

In the second step, WPO was performed inside the fume hood to destroy and eliminate organic matter from the extracted particles. Ferrous sulfate ($FeSO4{\cdot}7H_2O$) solution (20 mL) and 30% hydrogen peroxide (H_2O_2) solution (20 mL), known as Fenton reagent was utilized as the WPO catalysts for each sample. The Fenton solution was incubated at room temperature for at least 2 h prior to being use. The solutions were added to the beakers containing the extracted particles and allowed to wait for 10 min. The beakers were further placed on hotplates and digested at 70 °C. If residual organic matter was visible, an additional 10 mL of H_2O_2 was added to extend and complete the digestion process until no organic matter remained visible. After completing the digestion process, the particles were extracted using the density separation process. Lastly, the supernatant was passed through five size groups (0.05–0.25 mm, –0.5 mm, –1 mm, –2 mm, and –5 mm) using sieves for MP extraction

The $ZnCl_2$ solution was reused each time after density separation through filtration using a 1 µm polytetrafluoroethylene (PTFE) membrane, density checking, and adjustment (Rodrigues et al., 2018).

2.3. MP Identification and Characterization

All the isolated MP particles were observed and counted according to their shapes, sizes, and colors under a microscope (BH2, Olympus, Japan) by adjusting the magnifications at 10×, 40×, and 100×. The counted particles were classified into small MPs (SMPs: <1 mm) and large MPs (LMPs: 1–5 mm) for data interpretation (Eo et al., 2018). The proportions of shapes, sizes, colors, and polymers were calculated based on the number of MP particles. Fourier transform infrared spectroscopy (FTIR-4600 and FTIR-6600, JASCO Corp., Ltd., Japan) was implemented to map the polymer composition. JASCO's Spectra Mananger™ v.2.0, software was utilized to collect spectrum data. For each measurement, background measurements were performed utilizing a blank sample. 32 background scans were selected to generate spectra at a resolution of 8 cm^{-1}. The infrared wavenumbers were set in the range from 4,000 cm^{-1} to 550 cm^{-1} to detect the polymers. The obtained spectra were compared to the spectral reference library KnowItAll® Informatics System 2013, JASCO Edition (Bio-Rad Laboratories Inc., USA). Any unconfirmed MP particles were deduced from the counted particles. Scanning electron microscopy (SEM) (JSM-7600 F, JEOL, Japan) was utilized to observe the surface morphological characteristics of the MPs with an accelerating voltage of up to 15.00 kV. The distribution of chemical elements and mapping was investigated using energy-dispersive X-ray spectroscopy (EDX, JED-2300, JEOL, Japan). For SEM-EDX analysis, the particles were chosen randomly as representatives of the shapes, sizes, colors, and polymers. Each MP particle was coated with a thin film of evaporated platinum as light blocking aid using an ion sputtering instrument (FC-RTS, JFC-1600, JEOL, Japan). ImageJ v.1.52t was utilized for the physical measurements of MPs (Schneider et al., 2012).

2.4. Quality Control and Quality Assessment (QA/QC)

Before employing the $ZnCl_2$ solution for density separation, we conducted a recovery test for several polymers including polyethylene (PE), polypropylene (PP), polystyrene (PS),

polyethylene terephthalate (PET), polyvinyl alcohol (PVA) using NaCl (1.2 g/cm^3) and $ZnCl_2$ (1.5 g/cm^3) solutions following the protocol set out in Rodrigues et al., 2018 & 2020. The results showed a mean higher recovery rate by $ZnCl_2$ (95%) solution compared to NaCl (71.67%). Rodrigues et al., 2020 found similar recovery rate and concluded that all types of the environmentally found MPs could be recovered by the $ZnCl_2$ solution. Based on the findings, we employed $ZnCl_2$ for the density separation. Results are given supplementary material (Fig. S1). Throughout the sampling and laboratory analysis processes, we avoided external contamination. The plastic materials were replaced with metal and glass materials. When using plastic materials, they were inspected if MPs were generated from them. However, no MPs were found to be generated externally from the materials used in the laboratory. Cotton made laboratory coats, masks, and nitrile gloves were used. Deionized water was used to rinse all the equipment. The materials were rinsed thoroughly before, during, and after use. The $ZnCl_2$ solution was filtered each time prior to use by the PTFE membrane filter paper (pore size: 1 µm; diameter: 47 mm; Omnipore™, Made in Ireland). Procedural blanks and control checks were conducted during the experiment. No particles were observed in the controls from the fume hood spaces, wet filter papers or sample blanks. No external MP particles or airborne MP particles were found. Thus, we confirmed all the MP particles were extracted from the sediments. Extracted MP particles were stored in glass Petri dishes and/or glass vials covered with aluminum foil.

2.5. Mass Concentrations of MPs

Mass concentrations were measured by converting MP particle numbers, as mass is equivalent to the multiplication of particle volume and density (Eo et al., 2019). The measured average polymer density was 1.14 g/cm^3 in the present study. The non-fiber particle (fragment and

film) shapes were flat. The overestimation of mass for non-fiber particles was reduced by multiplying with 0.1 (Cozar et al., 2014; Eo at. al., 2019). The fiber morphotype particles were cylindrical, and the measured mean radius of the fiber particles was used to measure the mass concentration.

$$\text{Weight of MPs Non-Fiber Particles, } W_{MPs} = \frac{4}{3}\pi r^3 \times 1.14 \times \alpha \quad (1)$$

$$\text{Weight of MPs Fiber Particles, } W_{MPs} = \pi r^2 h \times 1.14 \quad (2)$$

where, r represents the radius of MP particles. Considering the size distributions of the extracted MP particles, the radius of individual MP particles was measured according to the size classes. For the non-fiber particles, the measured r values as per the particle size classes were as follows: 0.075 mm for 0.05–0.25 mm; 0.1875 mm for 0.25–0.5 mm; 0.375 mm for 0.5–1 mm; 0.75 mm for 1–2 mm; and 1.5 mm for 2–5 mm. For the fiber MP particles, the measured average radius was 20 µm, α represents the shape factor for the non-fiber particles (0.1 for fragment and film, respectively) (Cozar et. al., 2014, Eo et al., 2019); h is the measured length of each fiber particle.

2.6. Pollution Load Index, Polymeric Hazard Index, and Ecological Risk Assessment

Kabir et al., 2021 developed an MP pollution risk assessment model. The model was employed with minor changes of the parameter names— the term 'ecological risk index' was used instead of 'pollution risk index' to refer to the risk implications to a definite ecosystem compartment, that is, river sediment of riverine ecosystem in this study.

To assess the *PLI* for each station and river, the formulas are as follows:

$$PLI_i = C_i/C_o \quad (3)$$

$$PLI_{river} = \sqrt[n]{PLI_1 \times PLI_2 \times PLI_3 \cdots\cdots PLI_n}, \quad (4)$$

where, i represents a river station, n represents the station numbers for a river, C_i represents the abundance of MP particles at station i, C_o is the minimum mean background abundance value to be extracted from the available literature (the baseline concentration C_o = 288 n/kg was taken from Sagawa et al., 2018 due to the similar environmental and geographical context via email communication); PLI_i is the pollution load index at station i and PLI_{river} is the MP pollution load index for the river, which is the root of the station numbers for a river (n^{th} root) of the total MP pollution load indices multiplied together. Sites are polluted when PLI >1 (Tomlinson et al., 1980).

Furthermore, we assessed the PHI by utilizing MP abundances and polymeric hazard scores adopted from Lithner et al. (2011) for the identified MP polymers. Assessments were performed using the following formulas.

$$PHI_i = \sum_{j=1}^{m}\{(P_{ji}/\ C_i)\ \times S_j\} \quad (5)$$

$$PHI_{river} = \sqrt[n]{PHI_1 \times PHI_2 \times PHI_3 \ldots\ldots\ldots \times PHI_n}, \quad (6)$$

where, j is a type of polymer (e.g., polyethylene (PE), polypropylene (PP), polystyrene (PS), etc.); m represents the number of identified polymer types; P_{ji} represents the number of particles for each single polymer identified at station i, and S_j represents the hazard score for each polymer (for instance, the S_j scores for the specific polymer types were as follows: PE: 11, PP: 1, PS: 30, etc.;

hazard scores for each identified polymer are displayed in Table S2 as supplementary taken from Lithner et al. (2011); PHI_i is the cumulative polymeric hazard index at station *i;* PHI_{river} is the polymeric hazard for the rivers, which is the root of the station numbers for a river (n^{th} root) of the total polymeric hazard scores multiplied together.

Based on the *PLI* and *PHI*, the calculated ecological risks are as follows:

$$ERI_i = PHI_i \times PLI_i \quad (7)$$

$$ERI_{river} = \sqrt[n]{ERI_1 \times ERI_2 \times ERI_3 \ldots\ldots\ldots \times ERI_n}, \quad (8)$$

where, ERI_i is the MP pollution ecological risk index at station *i*, and ERI_{river} is the ecological risk for the river, which is *the n*th root of the total ecological risk scores multiplied together.

2.7. Data Analysis

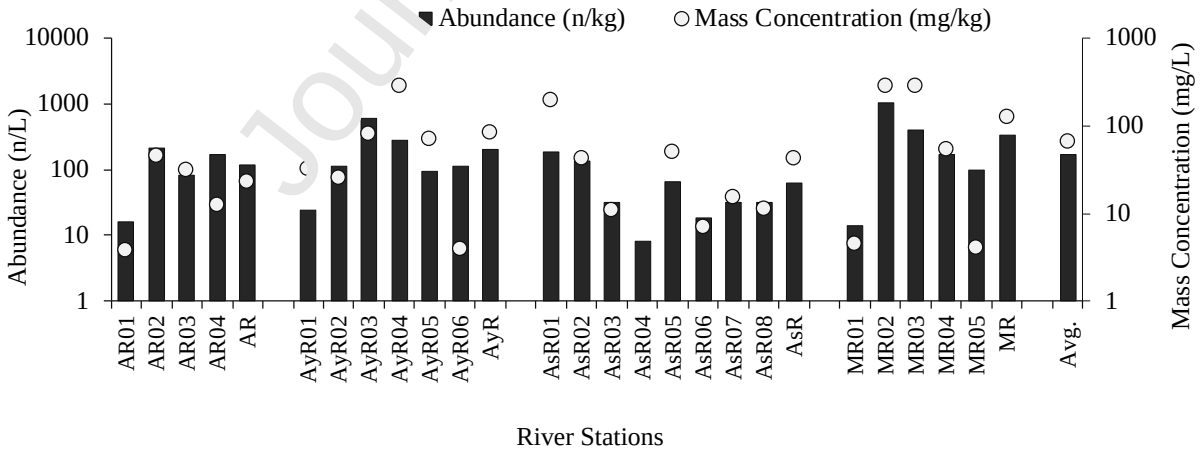
Microsoft Excel 2016 (16.0.13328.20350 (Microsoft Corp., USA) and IBM SPSS v25 (IBM Corp., Armonk, NY) was implemented for the statistical analysis. Descriptive analysis was conducted on the MP abundances and mass concentrations, i.e., the maximum, minimum, mean, median and standard deviation values. We used a non-parametric Kruskal Wallis H test to evaluate if there were significant differences in MP abundances, land-use (i.e., urban and residential, and agricultural, forests etc.) types, and population numbers among rivers due to the abnormal distribution of the data. In case of finding of significant difference after the Kruskal-Wallis test, a pairwise Wilcoxon test was used to identify which data produced the significant difference. The non-parametric Spearman correlation test was employed to determine the correlation MP abundance and mass concentrations; land-use types and MP abundances; identify the marker polymers;

ecological risks and polymeric toxicity; polymeric toxicity and MP abundances; MP abundances and ecological risks. The significance level (p) for the performed statistical tests was set at 0.05.

3. Results and Discussion

3.1. MP Abundances and Concentrations, Distribution and Land-use

All the selected stations of the rivers were observed to be contaminated with MPs. The abundances ranged from 8 to 1010 MP particles (n) per kilogram (kg) of sediment (dry weight). The lowest number of MPs was detected at station AsR05 (8 n/kg) of AsR, and the highest numbers were detected in MR02 (1010 n/kg) of MR. Overall, the average and median MP abundances were 167.29 ± 232.29 n/kg and 96 n/kg, respectively. The total number of extracted MP particles was 3896. Although MP abundances varied among the rivers, we found an insignificant difference in MP abundances among the rivers statistically (Kruskal Wallis H Test, p-value = 0.299 > 0.05).



However, the MR (Mean: 337.2±402.37 n/kg; Median: 168 n/kg) exhibited comparatively higher abundances than the others, followed by AyR (Mean: 205±214.4 n/kg; Median: 114 n/kg)>AR

(Mean: 119±87.9 n/kg; Median: 124 n/kg)>AsR (Mean: 63±62.27 n/kg; Median: 32) (Fig. 2). Overall, the sediments of the four small-scale Japanese rivers are vulnerable to MP pollution.

Fig. 2. Number-based abundances and mass concentrations of MPs and their distributions in sediments along the river stations.

In terms of distribution of land-use types, Kruskal Wallis H test results (p-values = 0.022 < 0.05) followed by the pairwise Wilcoxon test (p-value = 0.043 < 0.05) showed that the MR and AyR had significantly higher urban and residential land-use areas than the AR and AsR. On the other hand, no significant differences of agricultural areas were found among the rivers by (Kruskal Wallis H test, p-value = 0.538 > 0.05). Regarding the population numbers, although the Kruskal Wallis H Test result showed an insignificant differences of population numbers among the rivers (p-value = 0.5688 > 0.05), however, MR (Population Density: 1121.15 n/km^2) and AyR (Population density: 657.23 n/km^2) had higher population density than the AsR (Population Density: 115.75 n/km^2) and AR (Population Density: 20.71 n/km^2). And the urban and residential areas dominated MR and AyR was observed to have comparatively higher MP abundances than the forest and agriculture areas affected AR and AsR (Fig. 1 & 2; Table S1). On the other hand, the abundances and distributions of MPs differed among the (up-, mid-, and down-) stream stations (Fig. 1 and 2). Higher MP abundances were observed in the urban, residential, and agricultural dominated midstream (AR02, AyR03, and MR02) and downstream (AR04, AyR04–06; AsR07–08; MR03–05) stations than in the upstream stations, except for the AsR. The mixed areas of urban, residential, and agriculture-dominated upstream stations AsR01 and AsR02 also exhibited comparatively higher abundances. Overall, the land-use patterns displayed that the urban and residential as well as the mixed areas of urban and residential, and agricultural areas dominated midstream and downstream stations demonstrated higher abundances (Fig. 1 and 2). On the contrary, the upstream stations were

merely covered by non-point sources, that is, agriculture, forests etc. and they were resulted in lower MP abundances, that is, AR01 (16 n/kg), MR01 (14 n/kg), and AyR01 (24 n/kg). Thus, overall, the MP abundances across the stations indicated that the point-sources, that is, urban and residential land-use sources could release higher numbers of MPs in the river sediments. However, there were no significant strength of relationships statistically among MP abundances, land-use types, and population numbers. Spearman rank correlation showed insignificant strength (*p*-value = 0.133 > 0.05; r^2 = 0.323; df = 23) of relationship between urban and residential, and MP abundances. Similarly, an insignificant (Spearman rank correlation, *p*-value = 0.631 > 0.05; r^2 = -0.106; df = 23) strength of relationship was found between agricultural areas. Also, the correlational analysis results (Spearman rank correlation, *p*-value = 0.331 > 0.05; r^2 = 0.212; df = 23) between population numbers and MP abundances showed a weak relationship. This finding is consistent with previous reports suggesting that the urban and residential land-use affected stations posed higher MP abundances in river sediments, even though there were no significant land-use predictors statistically between MP abundance and catchment parameters (Baldwin et al., 2016; Corcoran et al., 2020; Dikareva and Simon, 2019; Tibbetts et al., 2018; Kapp and Yeatman, 2018; Klein et al., 2015). To conclude, we thought urban and residential land-use sources might be the major land-use sources for the occurrences of MPs in the small-scale Japanese river sediments reflecting the plastic uses and human activities.

The mass concentrations of MP particles varied from 0.86 to 283.26 mg with an average value of 65.37 ± 94.42 mg and median value of 30.91 mg per one kilogram (kg) of river sediment (Fig. 2). Overall, the MP mass concentrations did not differ significantly (Kruskal Wallis test; *p*-value = 0.5278 > 0.05). However, comparatively higher mass concentrations were found in urban and highly populated MR (Mean: 124.83 ± 143.61 mg/kg; Median: 54.44 mg/kg) and AyR (Mean:

82.66 ± 102 mg/kg; Median: 51.78 mg/kg) than the AsR (Mean: 41.78 ± 64.99 mg/kg; Median: 13.21 mg/kg) and AR (Mean: 22.92 ± 18.33 mg/kg; Median: 21.69 mg/kg) (Fig. 2; Table 1). A significant correlation (Spearman rank correlation, $p = 0.000 < 0.05$; $r^2 = 0.768$; $df = 23$) was observed between the numerical abundances and mass concentrations. As the mass of the MP particles was dependent on the particle volume and density (Eo et al., 2019), the correlation result indicated that a higher number of particles resulted in a higher mass being influenced by the particle shapes, sizes, and densities. We found large sized MPs (>1 mm) of fragments and films as well as the high-density particles in the riverine sediments which are discussed details in the section 3.2 and 3.6 (Fig. 3, 4 and 5; Table S2). Thus, the stations which had the higher abundances of MPs with large sized and high-density resulted in higher mass concentration. For instance, MR02 (1010 n/kg; 277.80 mg/kg) and AyR03 (608 n/kg; 80.53 mg/kg), had a higher number of particles than AyR04 (278 n/kg; 282.45 mg/kg), AsR01 (182 n/kg; 196.80 mg/kg), and MR03 (398 n/kg; 283.26 mg/kg); however, the MR02 and AyR03 had comparatively far lower mass concentrations in respect to of MP abundances (Fig. 2). Thus, the dominance of large sized and high-density MP particles resulted in higher mass concentrations consistently in relation to particle numbers along the rivers stations.

In addition, the MP particle characteristics (density, shape, and size), river geomorphology, and hydrodynamics are also important factors in understanding MPs settling in sediments (Besseling et al., 2017; Kooi et al., 2018; Mani et al., 2019; Nizzetto et al., 2016a). MP particle characteristics induced environmental behavior and deposition of MPs in the small-scale Japanese river sediments are discussed in the section 3.6. Furthermore, future investigations are required to explain river geomorphology and hydrodynamics-induced MP deposition in sediments for explicit understanding of abundances, distribution and land-use at the river catchment scales.

3.2. MP Characteristics, Occurrences and Sources

3.2.1. Shapes, Sizes, Colors and Polymers

Three shape types following— fragments, films, and fibers were observed for MPs extracted from the sediments. The MP fragments (46.36%) and films (41.22%) were the dominant shape characteristics of the extracted MP particles. Fibers occupied the rest of the proportions at 12.42%. From the distribution viewpoint, the proportions of each shape varied among river stations. For AR, fragments predominated upstream of AR01. The midstream stations (AR02 and AR03) were affected by both the fragments and films, and the downstream station AR04 was mostly affected by the fibers and fragments. In the AyR, the upstream and midstream stations were mostly polluted by MP fragments. The downstream stations of AyR (AyR04–AyR06) were polluted by fragments and films. Films (97.70%) predominated the AyR04. In the AsR, films were predominant MPs in the upstream AsR01, and fragments dominated in the next upstream stations AsR02–AsR05. Midstream stations from AsR06–AsR07 were observed to be dominated by fragments. The downstream stations (AsR08–AsR10) were observed to be affected by both fragments, films, and fibers. The MR upstream (MR01) and downstream (MR04 and MR05) stations were observed to be predominated by MP fragments. However, the midstream MR02–MR03 were affected by both the fragments and films. From the land-use point of view, films and fibers were mostly observed along the urban and residential land-use dominated stations, while fragments were present along all the river stations. Fig. 3 illustrates the shape-based MP distribution in the sediments along the river stations.

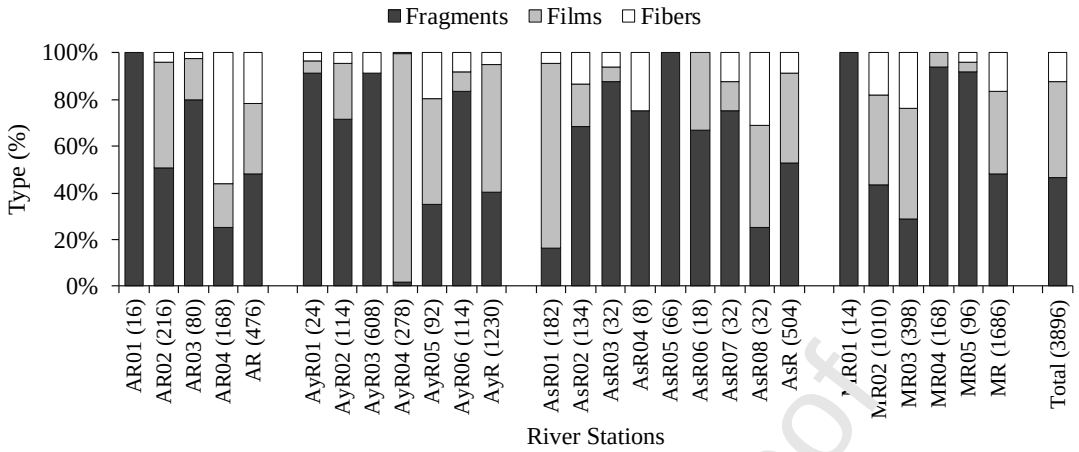


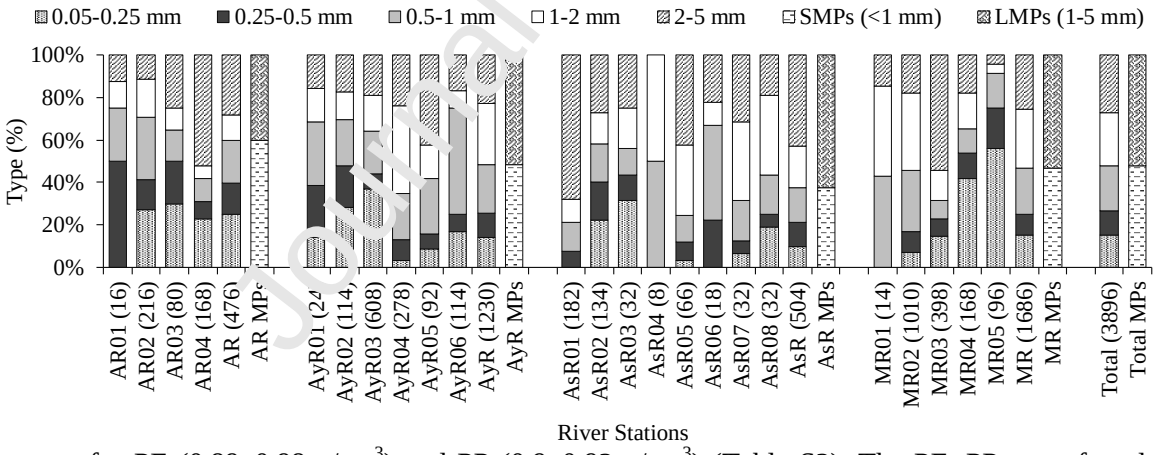
Fig. 3. Shape-based proportions of MPs of all the extracted particle numbers and their distributions among the river stations. Numbers in brackets represent the MP abundances.

The river sediment MPs were observed to be of various sizes. The MP particles of 2–5 mm (27.31%) size category predominated following the order: 1–2 mm (24.90%)>0.5–1 mm (21.30%)>0.25–0.5 mm (11.09)>0.05–0.25 mm (15.40%). However, the overall results revealed that both the small MPs (SMPs: <1 mm) and large MPs (LMPs: 1–5 mm) were similar, representing 47.79% and 52.21%, respectively, of the total number of MP particles (Fig. 4). The shape-size-based characterization exhibited that fragment MP particles were mostly SMPs, while the film and fiber MPs were LMPs (Fig. S2).

All the extracted MP particles sorted into visually obvious colors exhibited that transparent (29.00%) and white (27.00%) MPs occupied major proportions, followed by blue (16.79%), green (13.50%), red (6.62%), yellow (1.33%), gray (2.57%), and black (3.18%) (Fig. S3). Colorful MPs were observed with both bright and fresh, as well as dull and faded appearance.

Fig. 4. Size-based proportions of MPs among all of the extracted particle numbers and their distributions among the river stations. All size ranges are in millimeters (mm). Numbers in brackets represent the MP abundances.

FTIR analysis revealed 16 different polymers (Fig. 5). The results displayed that polyvinyl chloride (PVC) (26.18%), polyethylene (PE) (25.00%), and polypropylene (PP) (14.58%) were the major polymer types, followed by polystyrene (PS) (7.08%), polyvinyl alcohol (PVA) (7.80%), Nylon6 (2.57%), polyethylene terephthalate (PET) (6.37%), fluorinated ethylene propylene (FEP) (0.31%), acrylonitrile butadiene styrene (ABS) (0.26%), polymethylmethacrylate (PMMA) (0.77%), vinylon (1.69%), polybutylene terephthalate (PBT) (3.14%), polybutylene (PB) (1.69%), polycaprolactone (PCL) (1.18%), ethylene propylene diene monomer rubber (EPDM) (0.36%), and polyurethane (PUR) (0.72%). All the polymers were of higher density (>1 g/cm^3) than freshwater,



except for PE (0.89–0.98 g/cm^3) and PP (0.9–0.92 g/cm^3) (Table S2). The PE, PP were found as both fragments, films, and fibers; PVC, FEP, EPDM were observed as both the fragmented and films of diverse colors (transparent, white, blue, green, gray and black). Nylon 6 were found as transparent fragments and green fibers. PET was found as transparent fibers and black film. PS particles were found as red and white colored fragments. PVA were found as fragments and films in

transparent white, red, and grey colors. The shape and color-based MP polymers are provided in the supplementary information (Table S3). Fig. S4 shows the ATR-FTIR spectra for all known polymers.

From the distribution point of view, PE and PVA dominated the Awano River (AR); PE, PS, and PVC dominated the Asa River (AsR); PE, PP, PVA, and PVC were major in Ayaragi River (AyR); and PP, PET, and PVC were major in the Majime River (MR). The dominant PVC, PE, and PP particles are commonly observed along the river stations. More interestingly, a strong correlation was observed for the PVC (Spearman rank correlation, p-value = 0.001 < 0.05; r^2 = 0.649; df = 23) and PE (Spearman rank correlation, p-value = 0.002 < 0.05; r^2 = 0.613; df = 23) polymers with the distribution of MP abundances along the river stations. However, PE was not observed along all the stations (detected in 17 out of 23 stations), while PVC was observed along almost all the river stations (21 out of 23). Thus, the results suggested that the high-density PVC (1.16-1.58 g/cm^3) could be a potential marker polymer for MP pollution in river sediment environments. In addition to the predominant polymers, the overall non-predominating polymers also occupied large proportions in several river stations (e.g., PS in AR03, AsR01, AsR05, MR01, MR04; PVA in AR01–03, AyR01–03, and AyR06; Nylon 6 in AsR03–AR04, MR04–05; PET in MR03; Vinylon in AyR03; PBT in MR04–MR05; PCL in AR02). The distribution of the polymer types varied among the up-, mid-, and downstream stations, as well as the rivers. The polymeric compositions at each river's up-, mid-, and downstream stations differed, but revealed a combination of polymer types along the specific land-use dominated stations. The up- and mid-stream stations (AR01, AyR01–02, AsR01 and MR01) which were affected by the non-point agricultural sources and dominated by the forest areas, they differed in polymeric compositions than other stations. The mid-stream stations (AR02–03, AyR03, AsR05, and MR03) which were in the

urban, agricultural and forest interface were found having clear differences in polymeric compositions than other stations. The mid-stream AR02 showed differences in polymeric compositions which might be affected by the WWTP. Besides, the agricultural and urban areas affected AyR upstream stations AyR01–02; urban, residential and WWTP dominated mid-stream stations AsR02–04, and the AsR06–07 stations; and urban dominated downstream MR04–05 were observed having a combination of polymeric compositions which were identical. (Fig. 1 & 5). This suggested that the land-use specific sources might influence the occurrence of similar and specific MP polymers prominently along the river stations (Fig. 5).

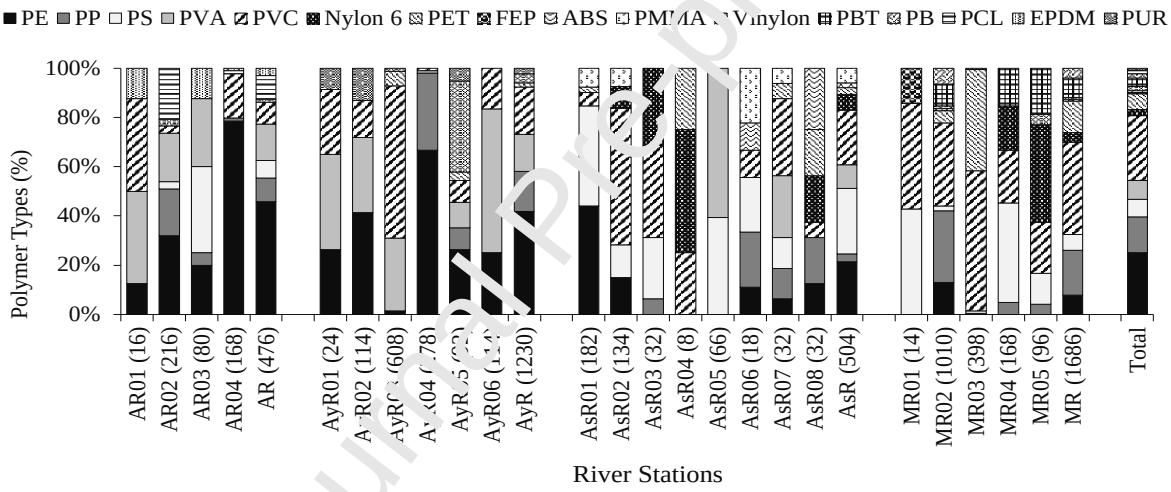
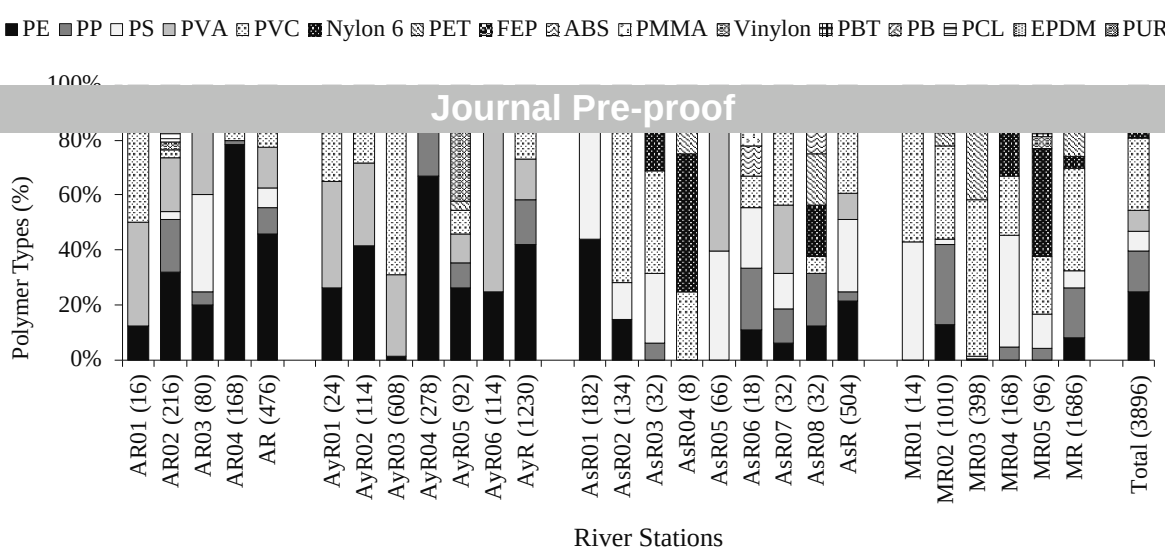


Fig. 5. Proportions of MP polymers among all of the extracted particle numbers and their distributions among the river stations. Numbers in brackets represent the MP abundances.

3.3 MP Sources and Occurrences

In this study, PVC, PE, and PP were the major polymers which constituted 65.76% of the total extracted MPs. They are the top three polymers of the major plastic types (PE, PP, PVC, and PS) with the prolonged history of production, use, and application in Japan. A comparison of plastic



production data in Japan from 2001 to 2020 revealed that approximately 13–9.6 million tons of plastic were produced, of which approximately 70% is represented by PVC, PE, PP, and PS (Japan Plastics Industry Federation (JPIF, 2020)). Plastic Europe (2020) reported that PVC, PE, PP, and PS constituted 65.24% of the total plastic demand worldwide in 2019. Overall, this presents a scenario of major polymers consumed in Japan and beyond. Currently, these residues are the major MP pollutant types in Japanese river sediments.

The predominant PVC fragments were ubiquitous along the river stations. PVC is utilized everywhere in households, piping, industrial, construction, urban, automotive, etc. The ubiquitous presence of PVC MPs along the river sediment indicated that both point (e.g., urban and residential) and non-point (e.g., agricultural) sources generated PVC MPs. Due to their high density, we inferred that PVC MPs were predestined to be sediments rather than floating on the surface water. Furthermore, PE, PP, and PS are generally referred to as 'single-use plastics (the disposable plastics products which are used once, or for a short period of time, before being thrown away or recycled; commonly used single-use plastic packaging items including e.g., grocery bags, food packaging, bottles, straws, containers, cups, cutlery, etc.)'. They are massively consumed globally, have a low useful life, and end up in waste streams and litter rapidly, leading to MP emissions (UNEP, 2018; GESAMP, 2016; Plastic Europe, 2020). Based on their distribution along the river stations, we concluded that point sources and non-point sources (domestic, industrial, commercial, agricultural, urban, and residential sources) might release them in these river systems (Fig. 5).

PVA and vinylon are polymers of the same monomer (Table S2). Vinylon is mostly synthesized from polyvinyl alcohol. The vinylon polymer was invented in 1939 in Japan and is commonly used in industries, agriculture, fisheries, textiles, clothing, ropes, and fishing nets (Sakurada, 1985). Vinylon was mostly observed in urban and residential areas especially in downstream stations of the AyR and MR (Fig.5). PVA was found mainly in the upstream of the AR, and both upstream and downstream of AyR, however, was absent in the MR, indicating the non-point sources (e.g., agricultural) might affect the occurrence. PET fibers were found mostly in the urban and residential land-use affected stations in the AyR and MR. Nylon 6 fibers were abundant in AsR03– AsR05 of AsR, and MR04–MR05 of MR, which were mostly affected by urban, residential, and agricultural land use. Based on the observation of all the identified Nylon 6 morphotypes, we inferred that they ensued from sacks and ropes utilized for agricultural, packaging, and household purposes. The point sources of domestic sewage, laundry drainage from washing machines, WWTPs, textiles, clothing, and non-point fishing tools, aquaculture nets, ropes, and agricultural and urban sources may release vast quantities of vinylon, PET, and nylon 6 fibers into Japanese rivers. Meanwhile, PBT was found as fragments solely in the urban area, as a higher number of populations dominated the downstream reaches of the MR, which may be derived from electronic, electrical, and automotive parts (Table S2).

EPDM is a durable synthetic rubber that was detected only in AR. ABS was mostly detected in the urban-affected downstream stations of AsR. Their automotive, construction, electrical, and household applications suggest that urban land use over residential areas might release EPDM and ABS particles into the rivers. The FEP in MR01 might be sourced from household applications. PMMA was only detected upstream, and downstream AsR might emerge from medical applications. PB was recorded in the MR02 midstream, affected mostly by point sources, that is, urban and

residential areas. This might emerge from personal care products and cosmetics. Details of the uses and applications of the MP polymers are presented in Table S2. Overall, various land use-based point and non-point sources may contribute to the release of MPs.

3.4. MPs in Small-scale Japanese River Sediments vs Other River Sediment Studies Worldwide

We compared the results of small-scale Japanese river sediment MP pollution with other river sediment studies around the world. The abundance comparison demonstrated similar order magnitudes of MP abundances in this study with the Brisbane River of Australia, Beijing River of China, Ganga River of India, Urban Rivers in the UK; higher values were observed than the Tibet Plateau Rivers, Qin River, Yongfeng River, and Yuehan River of China; and lower values than the Rhine and Main Rivers of Germany, Haihe River and Pearl River of China, and Nakdong River in South Korea. Fragments, films, and fiber-shaped MPs and PE, PP, PVC, PS, and PET were commonly reported in river sediments around the world, which were similar to the results of this study (Table 1). However, SMPs (<1 mm) were dominant in other river sediments around the world, while both SMPs and LMPs were similarly dominant in the Japanese small-scale rivers. Overall, the sediments of small-scale Japanese rivers were found MPs polluted relatively at a moderate abundance compared to other rivers around the world. On the other hand, several factors including hydrological and geomorphological characteristics; riverine basin areas; population, the catchment generated mismanaged plastics and MPs etc. might affect abundance in the small-scale Japanese rivers. Future studies are required to assess the factors for clear understanding why the MP abundances were higher and/or lower than other rivers around the world.

Table 1. Summary of microplastics abundances and characteristics in various riverine environments worldwide.

Study Areas	Abundance (n/kg) (d. w.)	Concentration (mg/kg)	Major Characteristics			Refrefences
			Size (mm)	Shape	Polymer	
Awano River, Japan	16—212[a]	3.54—44.74	0.05–1	Fragments, Films	PE, PP, PVA, PVC	This study
Ayaragi River, Japan	24—608[a]	3.94—282.45	1—5	Fragments, Films	PE, PP, PVA, PVC	This study
Asa River, Japan	8—182[a]	0.86—196.8	1—5	Fragments, Films	PE, PS, PVC	This study
Majime River, Japan	14—1010[a]	4.10—283.26	1—5	Fragments, Films	PVC, PET, PP	This study
Yongfeng River, China	5—72[a]	0.5–16.75	<1	Films	PE, PP	Rao et al., 2020
Yushan River, China	30—70[a]	3.5–53		Fibers, Films	PE, PP, PET	Niu et al., 2020
Urban Rivers, Shanghai, China	802 ± 594[b]		0.1–0.5	Spheres	PE, PET	Peng et al., 2018
Brisbane River, Australia	10—520[a]	0.18–129.20	<3	Films	PE	He et al., 2020
Rhine River, Germany	228—3763[a]	21.8–932	0.063—0.6	Fragments, spheres	PE, PP, PS	Klein et al., 2015
Main River, Germany	786—1368[a]	43.5—459	0.063—0.6	Fragments, spheres	PE, PP, PS	Klein et al., 2015
Beijiang River, China	178 ± 69—544 ± 107[a,b]				PE, PP	Wang et al., 2017
Wen-Rui Tang River, Wenzhou, Zhejiang Province, southeast China	18690—74800 (32947 ± 15342[a,b]		0.02–0.3	Fragments, Foams	PE, PP, PS, PES	Wang et al., 2018
Ganga River, India	99.27—409.86[a]	11.48–63.79			PET, PE, PP	Sarkar et al., 2019
Qin River, Beibu Gulf, China	0—97[a]		1–5	Fibers, sheets	PE, PP	Zhang et al., 2020
Maozhou River Hong Kong-Macao	35 ± 15—560 ± 70		0.1–1	Fragments	PE, PVC, PP, PS	Wu et al., 2020
Haihe River	1346—11,917 (4980 ± 2462)[a,b]		<1	Fibers	PE	Liu et al., 2020
Pearl River, China	80—9597[a]		0.05–0.5	Fibers	PE, PP	Lin et al., 2018
Wei River, China	360—1350[a]		0.075–0.5	Fibers	PE, PVC, PS	Ding et al., 2019
Nakdong River, South Korea	1971±6[a,b]		0.02–0.3	Fragments	PP, PE	Eo et al., 2019
Antua River	18—62[a]	2.6—71.4	--	Fragments, Fibers	PE, PP	Rodrigues et al., 2018
Tibet Plateau Rivers	50—195		<1	Fibers	PET	Jiang et al., 2019
Qiantang River, China	230 ± 60[b]		<0.5	Fragments, Fibers	PE	Fraser et al., 2020
Fengshan River, China	508-3987[a]		0.05–0.297	Fibers, Fragments	PE, PET, PA	Tien et al., 2020
Rhine River, Germany	0.26 ± 0.01—11.07 ± 0.6 × 10^{3} [a,b]		0.011–0.5		APV	Mani et al., 2019
Thames River, Ontario, Canada	6—2444[a]			Fibers, Fragments		Corcoran et al., 2020
Amzon Rivers, Brazil	417—8178[a]		0.063—1			Gerolin et al., 2020

[a] means the minimum to maximum value of microplastic abundance

[b] means the average abundance value of microplastics

[a,b] means the average value range of microplastic abundances from minimum to maximum

3.5. Chemical Weathering of MP Particles and Associated Metal Contaminants: Synergistic Hazard Potentials

MP weathering can be recognized from the FTIR spectrum (Rodrigues et al., 2018). We used PE and PP particles to analyze the weathering of MPs by FTIR spectra. The PE spectrum displays peaks around 2915, 2849, 1471, and 717 cm^{-1}; PP produces peaks around wave number regions 2950, 2916, 2850, 2839, 1460, and 1376 cm^{-1}. On the contrary, photo and oxidative degradation introduce new functional groups in the polymer chain through reactions with OH radicals, O, N oxides, and other photo-generated radicals. The carbonyl group is not characteristic of PE and PP, and forms from the introduction of oxygen into the polymer chain after exposure to visible (400–700 nm), high-energy UV radiation (290–400 nm) and/or atmospheric and aquatic oxygen. Thus, the carbonyl group (-C=O-) represents chemical weathering due to the introduction of oxygen into the polymer chain and display peaks around 1712–1736 cm^{-1} on FTIR spectra (da Costa et al., 2017; Prata et al., 2020; Rodrigues et al., 2018; Wang et al., 2017).

In comparison to the reference spectra for the examined PE and PP particles, we found the introduction of the carbonyl group at approximately 1712 and 1736 cm^{-1} in the PE fragment spectra, 1714 cm^{-1} in PP. The results suggested the presence of carbonyl groups formed by oxidation (Fig. S5). Thus, the introduction of a carbonyl group preliminarily indicated that the examined MPs underwent chemical weathering by oxidation (Prata et al., 2020; Rodrigues et al., 2018). An increase in degradation by chemical oxidation causes the surface of a plastic to crack, opening up new surfaces for further degradation processes to occur (da Costa et al., 2017; Prata et al., 2020; Rodrigues et al., 2018). To further analyze this perception, SEM analysis revealed the surface morphological characteristics. The results exhibited that the MPs had deeper cracks, pits, rifts, and

irregular and rough surfaces (Fig. 6). After MPs enter the environment, they undergo weathering processes, such as photo-oxidation, degradation, and mechanical abrasion, and changes appear on MP surfaces, such as cracks, pits, roughness, and irregular shapes (Corcoran et al., 2009; Gewert et al., 2015; Liu et al. 2020; Wang et al., 2017). In contrast, the surface of virgin MP particles should be smooth (Corcoran et al., 2009; Wang et al., 2017). Similar signs of weathering on MP surfaces have been observed in previous studies on river (Wang et al. 2017), beaches (Cooper and Corcoran, 2010; Corcoran et al. 2009), and lakes (Zbyszewski and Corcoran 2011, Zbyszewski et al., 2014). Hence, the finding of changes in the surfaces of MP particles suggested that the river sediment MPs underwent weathering processes and corroborates the speculation about the origin of MPs from the degradation or weathering of the large plastics in these fluvial settings.

While comparing the signs of weathering signs among the morphotypes, the results indicated that there were differences among the shapes. Fibers were observed with deep cracks, pits, rifts, and rough and irregular shapes, suggesting the highest degree of weathering (Fig. 6). Fragment surfaces were also observed with cracks, pits, and irregular surfaces. Comparatively, the surface of the MP films was observed having a relatively stable structure but still contained irregular and rough surfaces. We thought that the fibers underwent extensive weathering processes which is consistent with the previous studies that the fibers underwent extensive weathering processes (Corcoran et al., 2009; Wang et al., 2017).

Comparing the signs of weathering among the chemical composition of MPs, we inferred that there were differences between the morphological characteristics of PP and PE. The PE particles contained more pits, deeper cracks, prominent irregularities fractures, and rough surfaces than the PP particles. In particular, rifts usually appear on the surfaces of both the PE and PP; but

the PE contained more deeper cracks, pits, and prominent irregulates rather than on the surfaces of PP. This suggested that the PE were more vulnerable to weathering than the PP in the riverine sediments (Fig. 6). This supports the findings of Cooper and Corcoran (2010) that PE contains more pits and fractures than PP. In contrast, our results contradict the findings of Zbyszewski and Corcoran (2011) that PE particle surfaces were more resistant to weathering than PP on the beaches of Lake Huron. We believe that weathering processes are affected by several environmental conditions and factors such as water chemistry, waves, salinity, mechanical abrasion, oxidation and photo-oxidation, and aging processes. Thus, our contradictions might be related to the water chemistry, and environmental factors related to the study which might affect the weathering processes.

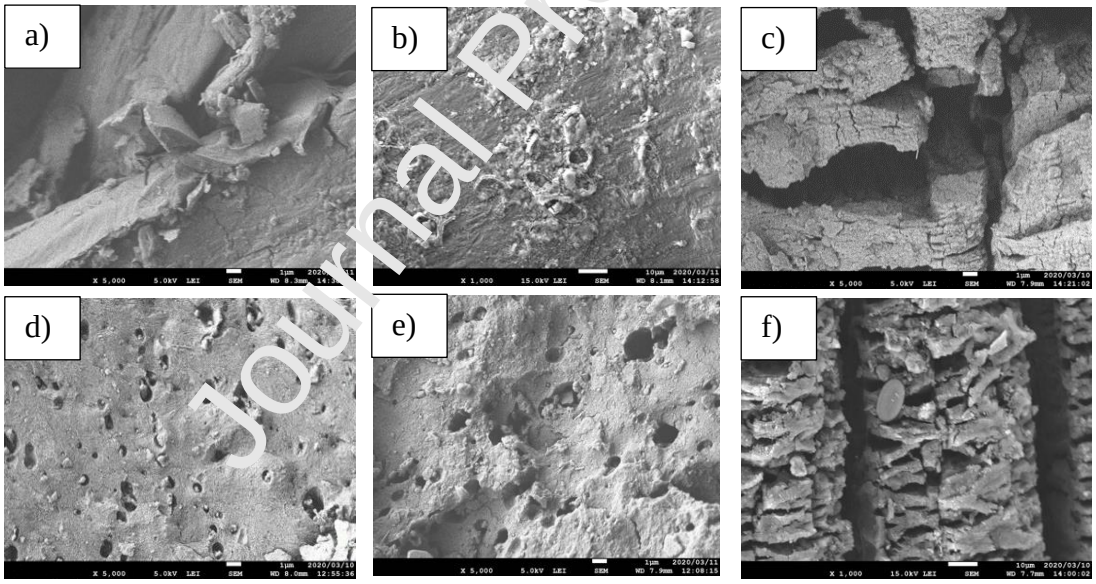


Fig. 6. Surface textures of the selected MPs by SEM-EDS analysis. a) PE fragment b) PE film c) PE fragment d) & e) PP fragment f) PE fiber

EDS analysis revealed that MP particles attached metal contaminants to their surfaces. MP particles of PE fragments contained Fe, Zn, and Ca; PE fibers contained Cu, Fe, Cr, and PE film contained Fe, Cu, Mg, and Na. The PP fragments contained Zn, Cu, Fe, Cr, Al, Na, and Cl. Some of them may come due to the materials used in the study, (e.g., $FeSO_4 \cdot 7H_2O$ and $ZnCl_2$). On the MP particles, Fe was common, but Zn was not. Thus, we thought that Fe and Zn might come from aquatic environments and/or also due to the used reagents. Future studies are recommended to confirm if the MPs contain such elements either from aquatic environments or reagents used in MP analysis. EDS also revealed titanium on the MP surfaces. Titanium appeared because of its use as a light-blocking aid for SEM-EDS analysis. Overall, MPs may take up metal contaminants from river aquatic environments. Fig. S6 illustrates the mapping of elemental composition on MP surfaces.

Overall, the MPs in the riverbed sediments underwent weathering processes and vectorized metal contaminants on their surfaces. The cracks and roughness of the weathered MP particles may facilitate to adsorb contaminants (Hartmann et al., 2017; Huffer et al., 2018; Liu et al., 2020; Mato et al., 2001; Wang et al., 2020; Yu et al., 2019). In this study, all the examined shapes and polymer types carried metal contaminants, while the fibers contained more toxic metals in this study. MP fibers are more toxic than other shapes, as they can be easily ingested and entangled by the biota and extremely mobile along the environmental compartments (Ziajahromi et al., 2017). Besides, studies found weathered MP particles might be more prone to cellular internalization and toxicity to biota by contact, uptake, and ingestion, contaminating the food web, and rapidly undergoing trophic transfer. Thus, weathered MP particles might be more harmful (Ramsperger et al., 2020; Zhou et al., 2020). Thus, they pose synergistic ecotoxicological hazards along these Japanese river aquatic environments. However, currently, our findings are hindered by limited information on metal concentrations attached to the MP surface as well as other pollutants. Therefore, we cannot

conclude if the metal contaminants cause significant threats; however, this creates concerns and demands for further investigations. Overall, these preliminary findings demand further investigations related to understanding weathering and vectoring the pollutants, surface oxidation, understanding MP particles aging process and degradation by carbonyl index under different spatial-temporal environmental conditions and processes, adsorption behavior of other toxic pollutants, and their implications for ecological toxicity in these river ecosystems.

3.6. Environmental Behavior of MPs in Sediment and Surface Water: Sediment as the sink

Both the fragments and films in shape, LMPs (1—5 mm) and SMPs (<1 mm) in size, and high-density polymeric MP particles than freshwater (>1 g/cm^3) (14 out of 16 identified polymers except PE and PP; 60.42% of the total extracted particles) were major in the river sediments. The sediment retained MP characteristics and types differed from those of the river surface water compartmental MPs found (SMP fiber <1 mm with low-density polymers dominated the surface water) at the same rivers and stations in our previous study by Kabir et al. (2021).

This is theoretically obvious that MP particles of high-density (>1.0 g/cm^3) polymers are prone to be settled easily in the freshwater environments and low-density particles float on the surface water or in the water column (Alam et al., 2019; Horton et al., 2017; Peng et al., 2018). We observed PVC (1.16–1.58 g/cm^3), PUR (1.2 g/cm^3), PMMA (1.17–1.2 g/cm^3), FEP (2.1–2.3 g/cm^3) as the high-density polymers which were absent in the surface water (Fig. 7). The dominance of high-density polymers in this study corroborates the results of several previous studies on river sediments (Table 1). Ballent et al. (2012), Chubarenko et al. (2016), and Kowalski et al. (2016) investigated the settling behavior of MPs with different high densities and suggested that the

settling velocity increased under the density regime in which higher density particles settled rapidly. Thus, we thought that the high-density MP particles were retained in the river sediment due to their settling behavior under the density regime, and this is one of the main reasons for their absence from the surface water in the studied Japanese rivers.

In contrast, the low-density MP polymer types, that is, PE and PP, were also a major component in the river sediments (Fig. 5 and 7). As reported worldwide, PE and PP are omnipresent MPs in different environmental compartments. As they are the most consumed plastics globally, the presence of PE and PP polymers in river sediments might occur in general (GESAMP, 2016; He et al. 2020; Plastics Europe, 2020). Previous studies have also reported the dominance of PE and PP in river sediments (Table 1). However, the question of interest is, how are they deposited in sediments? Studies have suggested that low-density PE and PP MPs are susceptible to weathering, biofilm formation and biofouling, attachment of organic matter and inorganic particles in sediments, aggregation of MPs into organic aggregates, and alteration of their density due to these factors (Anderson et al. 2016; Cole et al. 2011; Long et al. 2015; Morét-Ferguson et al., 2010). Cozar et al. (2014) and Morét-Ferguson et al. (2010) suggested that biofouling and attachment of organic matter alters low-density MPs, that is, PE and PP, to higher density, leading to sinking of the particles. Weathering facilitates the MP surface for biofilm formation and biofouling, adsorption and accumulation of pollutants, attachment of organic matter, breaking down further, and thus, increasing density, which might be the major reasons for the sinking and deposition of low-density MPs in sediments (Chubarenko et al. 2016; Kowalski et al., 2016; Van Cauwenberghe et al., 2015). In the present study, the SEM-EDS examined particles (PE and PP MPs) had undergone weathering. Based on our findings, we speculated that weathering might be a factor that facilitated the

deposition of low-density PE and PP MP particles in these river sediments among many other factors (e.g., biofouling, biodegradation, and mechanical forces etc.).

Several studies suggested that the physical properties of MPs (e.g., shape and size) might also cause different environmental behaviors (Chubarenko et al. 2016; Kooi et al., 2018; Kowalski et al. 2016). The physical properties revealed that SMP fragments, LMP film and fibers were major components in the river sediments (Fig. S2). More biofilms and foreign organic and inorganic materials are subjected to attachment to LMP surfaces, resulting in the bio-flocculation of LMPs. Even low-density LMP fragments and films can sink quickly owing to their large size and bio-flocculation (Zhang et al., 2020). All high-density MPs were found mostly as fragments and films (Table S2). Examining the settling behaviors of MPs, Chubarenko et al. (2016) revealed that high-density MP fragments took <18 h to settle through the water column, whereas PE fibers spent approximately 6–8 months in the euphotic zone before sinking, as a result of biofouling. The fragments and films might be less buoyant than the fibers and begin to sink due to biofouling (Chubarenko et al. 2016). Besides, Pohl et al. (2020) revealed that fibers were preferentially deposited in sediments trapped between settling sand grains. In this present study, the major component of the fibers was PET, which was inherently dense and prone to settle. Thus, overall, we thought that the MP particle characteristics (density, shapes and sizes) affected their retention in the river sediments. The river sediment compartment retained both distinctive and characteristics specific MPs due to environmental behavior of the particles as well as the common MPs in comparison to surface water. Thus, the small-scale Japanese river sediments acted as the prominent sink of MPs.

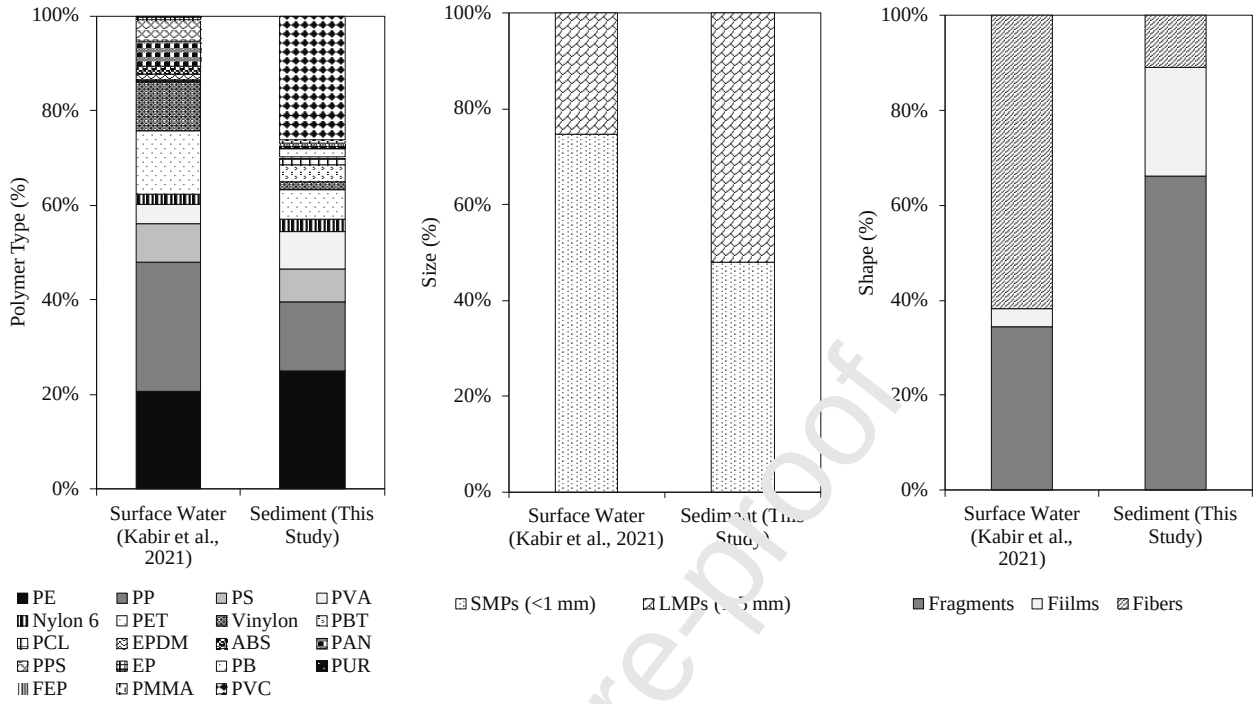


Fig. 7. Comparison of microplastic characteristics between the sediment and surface water of the small-scale Japanese rivers

3.7. MP Pollution Load Index (PLI), Polymeric Hazard Index (PHI), Ecological Risk Index (ERI) and Hotspots

When the *PLI* was greater than one (*PLI* >1), the site was considered contaminated (Tomlinson et al., 1980). In comparison to the background value (C_o = 288 n/kg) of Sagawa et al. (2018), the *PLI* results exhibited that the majority of river stations had lower *PLI* value with MP abundances. The midstream stations AyR03 of AyR and MR02–03 of the MR had higher *PLI* value i.e., *PLI* >1 (Fig. 8). This is due to the fact that the station which had higher MP abundances than the background value, the station had a high *PLI* value than other stations (Tomlinson et al., 1980). Overall, the small-scale river sediments were less contaminated than the compared abundance from Sagawa et al. (2018) in similar geographical context.

However, ecological risks are attributed not only to abundance, but also to polymer toxicity. Therefore, we considered ecological risks considering the *PLI*, the polymeric hazard index (*PHI*), and the ecological risk index (*ERI*) for a clear understanding of the ecological risks of MP contamination in river sediments. The categories of the *PHI and ERI* levels are employed in Table 2 to assess the ecological risks in this study utilizing from Hakanson, 1980; Peng et al., 2018; and Lithner et al., 2011.

The *PHI* values differed among river stations, indicating no to high level polymeric hazards based on the proportions of MP polymers found along the river stations. The MR, AyR and AsR rivers were found to pose high level of polymeric hazards, while the AR river ranked high level of polymeric hazards in terms of PHI values (Fig. 8; Table 2). The agricultural land-use dominating upstream stations AR01 and AR04 posed high-level polymeric hazards. The midstream stations AR02−AR03, which were affected by residential populations and urban areas, have been observed

to face low-to medium-level polymeric hazards. In the AyR, both the point (urban and residential) and non-point (agricultural) land-use sources dominating upstream and downstream stations (AyR01−AyR02, AyR04−06) posed high-level polymeric hazards, except for midstream AyR03. Similarly, all the stations of the AsR exhibited high levels of hazards caused by MP polymers, except for midstream AsR05 and upstream AsR01, which exhibited low and medium hazard levels, respectively. Both the point and non-point sources might influence the high polymeric hazard levels for the AsR. All the stations in the urban and higher populations dominated MR ranked high-level polymeric hazards by means of *PHI* values (Fig. 8; Table 2). As the polymeric hazard levels are the result of the proportion of found MP polymers, the stations that were affected by the highly toxic polymers (PVC, PUR, ABS, and Nylon 6 in this study) displayed high polymeric risks (Fig. 5 and 8). However, real MP abundances are not considered in assessing the *PHI*. For instance, AyR03 revealed higher MP abundances but displayed a low level of polymeric hazard. Even though the identified highly toxic polymers occupied lower proportions, these revealed high risks due to the individual hazard score of the specific polymers (Table S2). Thus, the elevated *PHI* values were largely due to the presence of toxic MP polymers and revealed insights into the highly toxic polymers observed in river sediments. The land uses suggested that highly toxic polymers could be released from both point and non-point land sources (Fig. 5; Fig. 1).

Table 2 Categories employed in the microplastics pollution loading index (*PLI*), polymeric hazard index (*PHI*), and ecological risk index (*ERI*).

ERI	***PHI***	**Risk category**
<150	<10	Low
150–300	10–100	Low-Medium
300–600	101–1,000	Medium
600–1,200	1,001–10,000	High
>1,200	>10,000	Very High

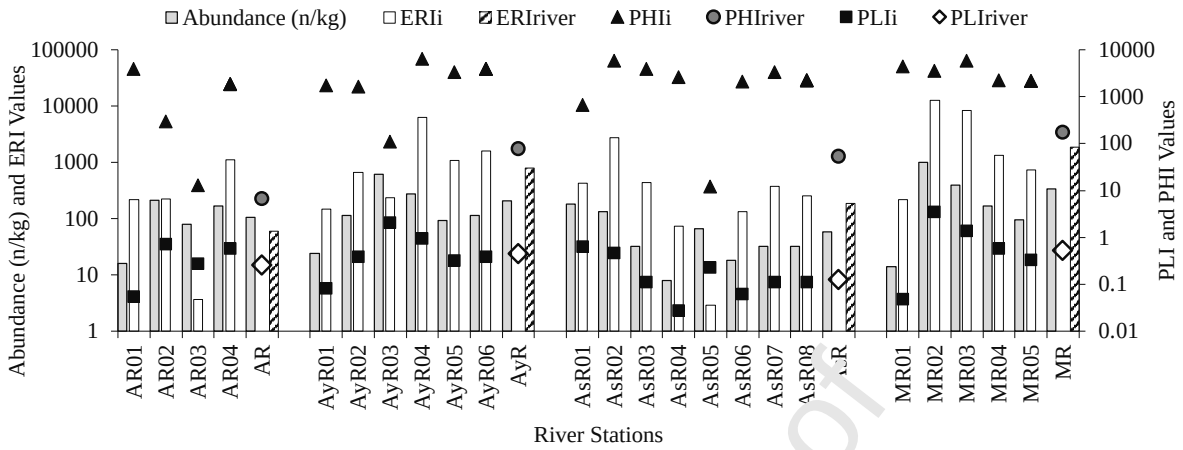


Fig. 8. Microplastic abundances, pollution load index (*PLI*), polymeric hazard score (*PHI*), ecological risk value (*ERI*), and their distributions among the river stations.

Based on the *PHI*, we cannot conclude that the high polymeric hazards imply high ecological risks. Rather, for the assessment of ecological risks (i.e., *ERI*), we introspect into the MP abundances and the obtained *PHI* values. The ERI_i values suggested low to very high ecological risk among the river stations (Fig. 8, Table 2). The downstream station AR04 of AR, upstream AyR02, and downstream reaches AyR04–06 of the AyR, upstream AsR03 of AsR, mid and downstream MR02–05 of MR ranked high to very high-level ecological risks. All stations with higher MP abundances didn't demonstrate high ecological risk levels by means of ERI_i (Table 2). For instance, AyR03, which contained higher MP abundances compared to other stations, posed a medium polymeric hazard by means of PHI_i value but a low-medium risk according to the ERI_i. In addition, all high polymeric hazard level posing stations, such as AR01, AyR01, AsR02, AsR05, AsR07, AsR10, and MR01 did not display high ecological risks consistently due to lower MP abundances (Fig. 9). We observed a significant correlation (Spearman rank correlation, *p*-value = 0.004 < 0.05; $r^2 = 0.569$; df = 23) between the *PHI* and *ERI*; and MP abundance and *ERI* (Spearman rank correlation, *p*-value = 0.0004 < 0.05; $r^2 = 0.6799$; df = 23). In contrast, we did not observe any

significant correlation between MP abundance and *PHI* (Spearman rank correlation, *p*-value = 0.9036 > 0.05; r^2 = -0.0267; df = 23). The results suggest that ecological risks *ERI* values are related to *PHI* and increase with MP abundance. Thus, the increased MP ecological risks were explicitly linked to the prevalence of MP abundance and their toxic polymers. However, this ecological risk assessment is limited, as the hazard scores for some of the polymers remain unknown (Table S2). This ecological risk assessment model can be utilized to assess the ecological risks for any ecosystem.

All the high-to very-high-risk ranked stations were mostly urban and residential point-sources land-use dominant except AR04, which was agricultural land-use dominated. All other non-point sources influenced the dominant stations (AR01–05, AyR01, AyR, AsR 01–09, MR01) and posed low to medium risks. Overall, the AyR and MR rivers exhibited high ecological risks, which were mostly governed by urban and population land use (Fig. 8). Thus, this study suggested that the point-sources, that is, urban and population land-use sources, might influence the occurrence of polymers, posing high ecological risks by releasing higher MP abundances and diverse polymers as well as the highly toxic polymers in the river sediments (Fig. 1 and 8). These findings of ecological risks of MP pollution slightly differed from those of Kabir et al. (2021), while both the point and non-point sources could pose high risks to the surface water of the same rivers. However, the stations that posed high ecological risks for the sediments across these river ecosystems were similar to the surface water, except for the non-point sources affected stations in surface water. MPs in the surface water are highly mobile across river systems to marine environments, while sediments are prone to accumulate MPs in fluvial ecosystems. Thus, urban and population-dominated areas could release higher amounts of MPs and the sediments could accumulate them. This could be one of the reasons why urban and residential land-use dominated stations posed

higher MP abundances and ecological risks of pollution. Based on the results of MP abundance and ecological risk assessment, we observed the following stations: AR04, AyR02, AyR04−AyR06, AsR03, and MR02−MR05 as MP pollution hotspots in the sediments of these rivers (Fig. 1). Thus, the urban and highly populated dominated areas were preferentially building up MP pollution hotspots in sediments along these small-scale riverine catchments. This is the reflection of plastic uses and human activity towards MP pollution occurrence, and posing the pollution induced ecological risks. Fig. 1 illustrates the geographic distribution of the risk zones. The risk zones and identified hotspots may be useful for developing practical approaches for pollution monitoring and management.

The assessed ecological risks possess implications for biotic and abiotic matrices in these riverine ecosystems, including humans, upon the exposure of MPs through various pathways (sediment –water and food commodities). MP pollutants may degrade the sediment habitat and food sources for aquatic organisms and contaminate the food web, and further trophic transfer of MP may occur in these aquatic ecosystems. Moreover, the identified toxic polymers (PVC, ABS, PUR, and PMMA) in the river sediments were mutagenic, carcinogenic, and endocrine disrupting, with long-lasting effects on aquatic organisms as well as humans (Gallo et al., 2018; Lithner et al., 2011). Furthermore, the weathering of MP particles and vectorized metal contaminants may enhance ecological hazards. Consequently, the MPs in sediments may pose numerous ecotoxicological threats to these riverine environments.

4. Conclusions

The river water-sediment interfaces of small-scale Japanese rivers were vulnerable to MP pollution. The riverine sediments accumulated mostly the fragments and film-shaped MPs of both large (LMPs: 1–5 mm) and small (SMPs: <1 mm) sized particles. Diverse polymers were observed, while PVC, PE, and PP were the most abundant. Sediment MPs underwent weathering processes and vectored metal contaminants, which are potential to cause synergistic hazards to these riverine ecosystems. The high-density MP polymers were dominant. We inferred that the high-density particles, shape and size characteristics influenced the deposition of MPs in the river sediments. PVC was identified as a potential MP pollution marker for the riverine sediments. In contrast to surface water, sediments preserved both common and distinctive microplastics. Thus, the riverine sediment compartment acted as microplastic sink. An assessment of ecological risks exhibited a risk level from low to very high. High ecological risk was linked to MP abundances and the presence of toxic polymers. Although both point and non-point sources might emit microplastics; however, ecological risks tended to be high in the urban and residential land-use sources affected areas due to their release of higher number MPs and toxic polymers. The result reflected that the plastic uses in higher human activity areas influenced MP pollution occurrences and posing high ecological risks. Thus, the urban areas and higher numbers of populations affected areas developed hotspots for MP pollution in sediment compartments of these riverine environments. The risk zones and pollution hotspots facilitated pollution monitoring and management priority zones. Overall, this comprehensive study filled the primary knowledge gaps regarding the MPs pollution in small-scale Japanese river sediments, revealed the environmental behavior of MPs and diverse MP characteristics in the riverine environments, shed light on sources-to-sinks phenomena and developed new insights into understanding riverine ecological threats. The current knowledge will contribute to water quality criteria policy making and legislation, developing practical intervention measures to protect rivers as well as control, management, and reduction of ecological risks of MP

pollution. Further investigations are required regarding environmental factors and processes influencing the deposition mechanisms of MPs in river sediments.

References:

Alam F.C., Sembiring E., Muntalif B.S., Suendo V., 2019. Microplastic distribution in surface water and sediment river around slum and industrial area (case study: Ciwalengke River, Majalaya district, Indonesia). Chemosphere, 224, pp. 637-645, https://doi.org/10.1016/j.chemosphere.2019.02.188

Allen, S., Allen, D., Phoenix, V.R., Roux, G.L., Jiménez, P.D., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. 12, 339–344. https://doi.org/10.1038/s41561-019-0335-5.

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62 (8), 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030

Arthur, C., Baker, J., & Bamford, H. (2009). Proceedings of the international research workshop on the occurrence, effects and fate of microplastic marine debris. Sept 9–11, 2008, NOAA Technical Memorandum NOS-OR&R30.

ASCE. Sediment and Aquatic Habitat in River Systems. Journal of Hydraulic Engineering. 1992;118(5):669–687. doi: 10.1061/(ASCE)0733-9429(1992)118:5(669).

Auta, H.S., Emenike, C.U., Fauziah, S.H., 2017. Distribution and importance of microplastics in the marine environment: a review of the sources, fate, effects, and potential solu- tions. Environ. Int. 102, 165–176. https://doi.org/10.1016/j.envint.2017.02.013.

Baldwin, A.K., Corsi, S.R., Mason, S.A., 2016. Plastic debris in 29 great lakes tributaries: relations to watershed attributes and hydrology. Environ Sci Technol 50 (19), 10377–10385. https://doi.org/10.1021/acs.est.6b02917.

Ballent A., Purser A., de Jesus Mendes P., Pando S., Thomsen L., 2012. Physical transport properties of marine microplastic pollution. Biogeosci. Discuss., 9, pp. 18755-18798, https://doi.org/10.5194/bgd-9-18755-2012

Besseling, E.; Quik, J. T. K.; Sun, M.; Koelmans, A. A. Fate of nano- and microplastic in freshwater systems: A modeling study. Environ. Pollut. 2017, 220, 540– 548. https://doi.org/10.1016/j.envpol.2016.10.001

Blettler M.C.M., Abrial E., Khan F.R., Sivri N., Espinola L.A., 2018. Freshwater plastic pollution: recognizing research biases and identifying knowledge gaps. Water Res., 143, pp. 416-424, https://doi.org/10.1016/j.watres.2018.06.015

Bordos G., Urbanyi B., Micsinai A., Kriszt B., Palotai Z., Szabo I., Hantosi Z., Szoboszlay S., 2019. Identification of microplastics in fish ponds and natural freshwater environments of the Carpathian basin, Europe. Chemosphere, 216, pp. 110-116. https://doi.org/10.1016/j.chemosphere.2018.10.110

Boucher, J. and Friot D. (2017). Primary Microplastics in the Oceans: A Global Evaluation of Sources. Gland, Switzerland: IUCN. 43pp.
Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., Thompson, R., 2011. Accumulation of microplastic on shorelines woldwide: sources and sinks. Envi- ron Sci Technol 45 (21), 9175–9179. https://doi.org/10.1021/es201811s.

Büks, F.; Kaupenjohann, M. Global concentrations of microplastics in soils – a review. Soil 2020, 6, 649– 662, https://doi.org/10.5194/soil-6-649-2020

Cheung, P.K., Hung, P.L. & Fok, L. River Microplastic Contamination and Dynamics upon a Rainfall Event in Hong Kong, China. Environ. Process. 6, 253–264 (2019). https://doi.org/10.1007/s40710-018-0345-0

Chubarenko, A. Bagaev, M. Zobkov, E. Esiukova. On some physical and dynamical properties of microplastic particles in marine environment. Mar. Pollut. Bull., 108 (1–2) (2016), pp. 105-112, https://doi.org/10.1016/j.marpolbul.2016.04.048

Cole, M., Lindeque, P., Halsband, C., Galloway, T.S., 2011. Microplastics as contaminants in the marine environment: a review. Mar. Pollut. Bull. 62 (12), 2588–2597. https://doi.org/10.1016/j.marpolbul.2011.09.025

da Costa J.P., Duarte A.C., Rocha-Santos T.A.P., 2017. Microplastics – occurrence, fate and behaviour in the environment. Compr. Anal. Chem. (2017), pp. 1-24, https://doi.org/10.1016/bs.coac.2016.10.004

Ding, L., Mao, R.F., Guo, X., Yang, X., Zhang, Q., Yang, C., 2019. Microplastics in surface waters and sediments of the Wei River, in the northwest of China. Sci. Total Environ. 667, 427–434. https://doi.org/10.1016/j.scitotenv.2019.02.332.

Coppock R.L., Cole M., Lindeque P.K., Queiros A.M., Galloway T.S., 2017. A small-scale, portable method for extracting microplastics from marine sediments. Environ. Pollut., 230, pp. 829-837, https://doi.org/10.1016/j.envpol.2017.07.017

Cooper D.A., Corcoran P.L., 2010. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai Hawaii. Mar. Pollut. Bull., 60 (5), pp. 650-654. https://doi.org/10.1016/j.marpolbul.2009.12.026

Corcoran P.L., Biesinger M.C., Grifi M., 2009. Plastics and beaches: a degrading relationship. Mar. Pollut. Bull., 58 (1), pp. 80-8. https://doi.org/10.1016/j.marpolbul.2008.08.022

Corcoran P.L., Belontz S.L., Ryan K., Walzak M.J., 2020. Factors controlling the distribution of microplastic particles in benthic sediment of the Thames River, Canada. Environ. Sci. Technol., 54, pp. 818-825. https://doi.org/10.1021/acs.est.9b04896

Cozar, A., Echevarria, F., Gonzalez-Gordillo, J.I., Irigoien, X., Ubeda, B., Hernandez-Leon, S., Palma, A.T., Navarro, S., Garcia-de-Lomas, J., Ruiz, A., Fernandez-de-Puelles, M.L., Duarte, C.M., 2014. Plastic debris in the open ocean. Proc. Natl. Acad. Sci. U. S. A. 111 (28), 10239–10244. https://doi.org/10.1073/pnas.1314705111.

Conley, K., Clum, A., Deepe, J., Lane, H., Beckingham, B., 2019. Wastewater treatment plants as a source of microplastics to an urban estuary: removal efficiencies and loading per capita over one year. Water Res X 3, 100030. https://doi.org/10.1016/j.wroa.2019.100030.

de Sá LC, Oliveira M, Ribeiro F, Rocha TL, Futter MN: Studies of the effects of microplastics on aquatic organisms: What do we know and where should we focus our efforts in the future? Sci. Total Environ., 645, 1029–1039, 2018. https://doi.org/10.1016/j.scitotenv.2018.07.207

Dikareva N., Simon K.S., 2019. Microplastic pollution in streams spanning an urbanisation gradient. Environ. Pollut., 250, pp. 292-299, https://doi.org/10.1016/j.envpol.2019.03.105

Dris R., Gasperi J., Tassin B., 2018. Sources and Fate of Microplastics in Urban Areas: A Focus on Paris Megacity. In: Wagner M., Lambert S. (eds) Freshwater Microplastics. The Handbook of Environmental Chemistry, vol 58. Springer, Cham. https://doi.org/10.1007/978-3-319-61615-5_4.

Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater sys- tems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. Water Res. 75, 63–82. https://doi.org/10.1016/j. watres.2015.02.012.

van Emmerik, T., Schwarz, A., 2020. Plastic debris in rivers. WIREs Water 7 (1). https://doi.org/10.1002/wat2.1398n.

Eo, S., Hong, S.H., Song, Y.K., Lee, J., Lee, J., Shim, W.J., 2018. Abundance, composition, and distribution of microplastics larger than 20 μm in sand beaches of South Korea. Envi- ron. Pollut. 238, 894–902. https://doi.org/10.1016/j.envpol.2018.03.096.

Eo, S., Hong, S.H., Song, Y.K., Han, G.M., Shim, W.J., 2019. Spatiotemporal distribution and annual load of microplastics in the Nakdong River, South Korea. Water Res. 160, 228–237. https://doi.org/10.1016/j. watres.2019.05.053.

Eriksen M., Mason S., Wilson S., Box C., Zellers A., Edwards W., Farley H., Amato S., 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes. Mar. Pollut. Bull., 77, pp. 177-182, https://doi.org/10.1016/j.marpolbul.2013.10.007

Fischer E.K., Paglialonga L., Czech E., Tamminga M., 2016. Microplastic pollution in lakes and lake shoreline sediments – a case study on Lake Bolsena and Lake Chiusi (Central Italy). Environ. Pollut., 213 (2016), pp. 648-657. https://doi.org/10.1016/j.envpol.2016.03.012

Frias J, Nash R, Pagter E, O'Connor I: Standardised protocol for monitoring microplastics in sediments. JPI-Oceans BASEMAN project, 2018. doi:10.13140/ RG.2.2.36256.89601/1. https://www.jpi-oceans.eu/ sites/jpi-oceans.eu/files/public/Microplastics/JPI%20 Oceans%20Final%20Project%20Report%20-%20 BASEMAN.pdf [accessed on 17 February 2019]

Fraser M.A., Chen L., Ashar M., Huang W., Zeng J., Zhang C., Zhang D., 2020. Occurrence and distribution of microplastics and polychlorinated biphenyls in sediments from the Qiantang River and Hangzhou Bay. China. Ecotoxicol. Environ. Saf., 196, p. 110536, https://doi.org/10.1016/j.ecoenv.2020.110536

Gallo, F., Fossi, C., Weber, R., Santillo, D., Sousa, J., Ingram, I., Nadal, A., Romano, D., 2018. Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. Environ. Sci. Eur. 30 (1), 13. https://doi.org/10.1186/s12302-018-0139-z.

Galloway, T.S., 2015. Micro- and nano-plastics and human health. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer, Cham https://doi.org/10.1007/978-3-319-16510-3_13.

GESAMP (2016). "Sources, fate and effects of microplastics in the marine environment: part two of a global assessment" (Kershaw, P.J., and Rochman, C.M., eds). (IMO/ FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Rep. Stud. GESAMP No. 93, 220 p.

Gerolin C.R., Pupim F.N., Sawakuchi A.O., Grohmann C.H., Labuto G., Semensatto D., 2020. Microplastics in sediments from Amazon rivers. Brazil. Sci. Total Environ., 749, p. 141604, https://doi.org/10.1016/j.scitotenv.2020.141604

Gewert B, Plassmann MM, MacLeod M: Pathways for degradation of plastic polymers floating in the marine environment. Environ. Sci. Process. Impacts, 17(9), 1513–1521, 2015. https://doi.org/10.1039/C5EM00207A

Hakanson L.J., 1980. An ecological risk index for aquatic pollution control.a sedimentological approach
Water Res., 14 (8) (1980), pp. 975-1001, https://doi.org/10.1016/0043-1354(80)90143-8.

He B., Goonetilleke A., Ayoko G.A., Rintoul L., 2019. Abundance, distribution patterns, and identification of microplastics in Brisbane River sediments, Australia. https://doi.org/10.1016/j.scitotenv.2019.134467

Henry, B., Laitala, K., Klepp, I.G., 2019. Microfibres from apparel and home textiles: pros- pects for including microplastics in environmental sustainability assessment. Sci. Total Environ. 652, 483–494. https://doi.org/10.1016/j.scitotenv.2018.10.166.

Hernandez, E., Nowack, B., Mitrano, D.M., 2017. Polyester textiles as a source of microplastics from households: a mechanistic study to understand microfiber release during washing. Environ. Sci. Technol., 51 (12), 7036–7046. https://doi.org/10.1021/acs.est.7b01750.

Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190.

Horton, A.A., Dixon, S.J., 2018. Microplastics: an introduction to environmental transport processes. Wiley Interdiscip. Rev. Water 5 (2). https://doi.org/10.1002/wat2.1268.

Hu, L., Chernick, M., Hinton, D.E., Shi, H., 2018. Microplastics in small waterbodies and tad- poles from Yangtze River Delta, China. Environ Sci Technol 52 (15), 8885–8893. https://doi.org/10.1021/acs.est.8b02279.
Huang, Y., Liu, Q., Jia, W., Yan, C., Wang, J., 2020. Agricultural plastic mulching as a source of microplastics in the terrestrial environment. Environ. Pollut. 260, 114096. https://doi.org/10.1016/j.envpol.2020.114096.

Hahladakis J.N., Velis C.A., Weber R., Iacovidou E., Purnell P., 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard. Mater., 344, pp. 179-199. https://doi.org/10.1016/j.jhazmat.2021.125811

Isobe, A., Uchida, K., Tokai, T., Iwasaki, S., 2015. East Asian seas: a hot spot of pelagic microplastics. Mar. Pollut. Bull. 101 (2), 618–623. https://doi.org/10.1016/j. marpolbul.2015.10.042.

Koelmans, A.A., Besseling, E., Foekema, E., Kooi, M., Mintenig, S., Ossendorp, B.C., Redondo-Hasselerharm, P.E., Verschoor, A., van Wezel, A.P., Scheffer, M., 2017. Risks of plastic debris: unravelling fact, opinion, perception, and belief. Environ Sci Technol 51 (20), 11513–11519. https://doi.org/10.1021/acs.est.7b02219.

Kowalski N., Reichardt A.M., Waniek J.J., 2016. Sinking rates of microplastics and potential implications of their alteration by physical, biological, and chemical factors. Mar. Pollut. Bull., 109, pp. 310-319. https://doi.org/10.1016/j.marpolbul.2016.05.064

Llorca M., Schirinzi G., Martínez M., Barceló D., Farré M., 2018. Adsorption of perfluoroalkyl substances on microplastics under environmental conditions. Environ. Pollut., 235, pp. 680-691, https://doi.org/10.1016/j.envpol.2017.12.075

Li J., Zhang K., Zhang H., 2018. Adsorption of antibiotics on microplastics. Environ. Pollut., 237, pp. 460-467, https://doi.org/10.1016/j.envpol.2018.02.050

Luo, W., Su, L., Craig, N.J., Du, F., Wu, C., Shi, H., 2019. Comparison of microplastic pollution in different water bodies from urban creeks to coastal waters. Environ. Pollut. 246, 174–182. https://doi.org/10.1016/j.envpol.2018.11.081.

Lin L., Zuo L.Z., Peng J.P., Cai L.Q., Fok L., Yan Y., Li H.X., Xu X.R., 2018. Occurrence and distribution of microplastics in an urban river: a case study in the Pearl River along Guangzhou City, China. Sci. Total Environ., 644, pp. 375-381. https://doi.org/10.1016/j.scitotenv.2018.06.327

Mato Y., Isobe T., Takada H., Kanehiro H., Ohtake C., Kaminuma T. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol., 35 (2001), pp. 318-324, https://doi.org/10.1021/es0010498

Hartmann N.B., Rist S., Bodin J., Jensen L.H., Schmidt S.N., Mayer P., Meibom A., Baun A.

Microplastics as vectors for environmental contaminants: exploring sorption, desorption, and transfer to biota. Integr. Environ. Assess. Manag., 13 (3) (2017), pp. 488-493, https://doi.org/10.1002/ieam.1904

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347, 768–771. https://doi.org/10.1126/science.1260352.

JPIF, 2020. The Japan Plastics Industry Federation (JPIF): Statistics of The Japan Plastics In- dustry Federation, 2018. http://jpif.gr.jp/english/statistics/index.html [accessed on 25th February 2021].

Jiang, C., Yin, L., Li, Z., Wen, X., Luo, X., Hu, S., Yang, H., Long, Y., Deng, B., Huang, L., Liu, Y., 2019. Microplastic pollution in the rivers of the Tibet Plateau. Environ. Pollut. 249, 91–98. https://doi.org/10.1016/j.envpol.2019.03.022.

Kabir, A.H.M.E.; Sekine, M.; Imai, T.; Yamamoto, K.; Kanno, A., Higuchi, T. Assessing small-scale freshwater microplastics pollution, land-use, source-to-sink conduits, and pollution risks: Perspectives from Japanese rivers polluted with microplastics. Sci. Total Environ. 2021, 768, 144655. https://doi.org/10.1016/j.scitotenv.2020.144655

Kapp, K.J., Yeatman, E., 2018. Microplastic hotspots in the Snake and Lower Columbia riv- ers: a journey from the Greater Yellowstone Ecosystem to the Pacific Ocean. Environ. Pollut. 241, 1082–1090. https://doi.org/10.1016/j.envpol.2018.06.033

Kataoka, T., Nihei, Y., Kudou, K., Hinata, H., 2019. Assessment of the sources and inflow processes of microplastics in the river environments of Japan. Environ. Pollut. 244, 958–965. https://doi.org/10.1016/j.envpol.2018.10.111.

Klein, S., Worch, E., Knepper, T.P., 2015. Occurrence and spatial distribution of microplastics in river shore sediments of the Rhine-Main area in Germany. Environ Sci Technol 49 (10), 6070–6607. https://doi.org/10.1021/acs.est.5b00492.

Kooi, M.; Besseling, E.; Kroeze, C.; van Wezel, A. P.; Koelmans, A. A. Modeling the Fate and Transport of Plastic Debris in Freshwaters: Review and Guidance. In Freshwater microplastics: Emerging environmental contaminants?; Wagner, M., Lambert, S., Besseling, E., Biginagwa, F. J., Eds.; The handbook of environmental chemistry/founded by Otto Hutzinger ; editors-in-chief: Damià Barceló, Andrey G. Kostianoy ; volume 58; Springer Open: Cham, 2018; pp 125– 152. https://doi.org/10.1007/978-3-319-61615-5_7

Kramm J., Völker C. (2018) Understanding the Risks of Microplastics: A Social-Ecological Risk Perspective. In: Wagner M., Lambert S. (eds) Freshwater Microplastics. The Handbook of Environmental Chemistry, vol 58. Springer, Cham. https://doi.org/10.1007/978-3-319-61615-5_11

Kumar, R.; Sharma, P.; Bandyopadhyay, S. Evidence of microplastics in wetlands: Extraction and quantification in freshwater and coastal ecosystems. J. Water Process Eng. 2021, 40, 101966. https://doi.org/10.1016/j.jwpe.2021.101966

Lambert, S., Wagner, M., 2018. Microplastics Are Contaminants of Emerging Concern in Freshwater Environments: An Overview. In: Wagner M., Lambert S. (eds) Freshwater

Microplastics. The Handbook of Environmental Chemistry, vol 58. Springer, Cham. https://doi.org/10.1007/978-3-319-61615-5_1.

Li, J., Liu, H., Paul Chen, J., 2018. Microplastics in freshwater systems: a review on occurrence, environmental effects, and methods for microplastics detection. Water Res. 137, 362–374. https://doi.org/10.1016/j.watres.2017.12.056.

Lithner, D., Larsson, A., Dave, G., 2011. Environmental and health hazard ranking and as- sessment of plastic polymers based on chemical composition. Sci. Total Environ. 409 (18), 3309–3324. https://doi.org/10.1016/j.scitotenv.2011.04.038.

Liu P., Zhan X., Wu X., Li J., Wang H., Gao S., 2020. Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks. Chemosphere, 242, 125193. https://doi.org/10.1016/j.chemosphere.2019.125193

Liu Y., Zhang J., Tang Y., He Y., Li Y., You J., Breider F., Tao S., Liu W., 2020. Effects of anthropogenic discharge and hydraulic deposition on the distribution and accumulation of microplastics in surface sediments of a typical seagoing river: the Haihe River. J. Hazard. Mater., 404, p. 124180, https://doi.org/10.1016/j.jhazmat.2020.124180

Long M., Moriceau B., Gallinari M., Lambert C., Huvet A., Raffray J., Soudant P., 2015. Interactions between micro-plastics and phytoplankton aggregates: impact on their respective fates. Mar. Chem., 175, pp. 39-46. https://doi.org/10.1016/j.marchem.2015.04.003

Mani T., Primpke S., Lorenz C., Gerdts G., Burkhardt-Holm P., 2019. Microplastic pollution in benthic midstream sediments of the Rhine River. Environ. Sci. Technol., 53 (10), pp. 6053-6062. https://doi.org/10.1021/acs.est.9b01363

Masura, J., et al. 2015. Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments. NOAA Technical Memorandum NOS-OR&R-48.

Murphy, F., Ewins, C., Carbonnier, F., Quinn, B., 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environ Sci Technol 50 (11), 5800–5808. https://doi.org/10.1021/acs.est.5b05416.

Napper, I.E., Thompson, R.C., 2016. Release of synthetic microplastic plastic fibres from domestic washing machines: effects of fabric type and washing conditions. Mar. Pollut. Bull. 112 (1–2), 39–45. https://doi.org/10.1016/j.marpolbul.2016.09.025.

Nizzetto, L., Bussi, G., Futter, M.N., Butterfield, D., Whitehead, P.G., 2016a. A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. Environ Sci Process Impacts 18 (8), 1050–1059. https://doi.org/10.1039/C6EM00206D

Nizzetto, L., Futter, M., Langaas, S., 2016b. Are agricultural soils dumps for microplastics of urban origin? Environ Sci Technol 50 (20), 10777–10779. https://doi.org/10.1021/acs.est.6b04140

Niu S., Wang X., Rao Z., Zhan N., 2021. Microplastics present in sediments of Yushan River: a case study for urban tributary of the Yangtze River. Soil and Sediment Contamination: Int. J., https://doi.org/10.1080/15320383.2020.1841731

O'Connor J.D., Mahon A.M., Ramsperger A.F.R.M., Trotter B., Redondo-Hasselerharm P.E., Koelmans A.A., Lally H.T., Murphy S., 2020. Microplastics in freshwater biota: a critical review of isolation, characterization, and assessment methods. Global Challenges, 4 (6), p. 1800118, https://doi.org/10.1002/gch2.201800118

Prata J.C., Reis V., Paço A., Martins P., Cruz A., da Costa J.P., Duarte A.C., Rocha-Santos T., 2020. Effects of spatial and seasonal factors on the characteristics and carbonyl index of (micro)plastics in a sandy beach in Aveiro Portugal. Sci. Total Environ., 709, 135892. https://doi.org/10.1016/j.scitotenv.2019.135892

Villarrubia-Gómez P., Cornell S.E., Fabres J., 2018. Marine plastic pollution as a planetary boundary threat – the drifting piece in the sustainability puzzle. Mar. Policy, 96, pp. 213-220. https://doi.org/10.1016/j.marpol.2017.11.035

Peng, L., Fu, D., Qi, H., Lan, C.Q., Yu, H., Ge, C., 2020. Micro- and nano-plastics in marine environment: source, distribution and threats - a review. Sci. Total Environ. 698, 134254. https://doi.org/10.1016/j.scitotenv.2019.134254.

Peng G., Xu P., Zhu B., Bai M., Li D., 2018. Microplastics in freshwater river sediments in Shanghai, China: a case study of risk assessment in mega-cities Environ. Pollut., 234, pp. 448-456, https://doi.org/10.1016/j.envpol.2017.11.034

Plastics Europe, 2020. Plastics- the Facts 2020. An Analysis of European Latest Plastics Production, Demand and Waste Data. Plastics Europe, Brussels, Belgium.
Pohl, F.; Eggenhuisen, J. T.; Kane, I. A.; Clare, M. A., 2020. Transport and Burial of Microplastics in Deep-Marine Sediments by Turbidity Currents. Environ. Sci. Technol. 2020, 54 (7), 4180– 4189, https://doi.org/10.1021/acs.est.9b07527

Rao, Z., Niu, S., Zhan, N. et al. Microplastics in Sediments of River Yongfeng from Maanshan City, Anhui Province, China. Bull Environ Contam Toxicol 104, 166–172 (2020). https://doi.org/10.1007/s00128-019-02771-2

Ramsperger A.F.R.M., Narayana V.K.B., Gross W., Mohanraj J., Thelakkat M., Greiner A., Schmalz H., Kress H., Laforsch C. Environmental exposure enhances the internalization of microplastic particles into cells. Sci. Adv., 6 (2020), Article eabd1211, https://doi.org/10.1126/sciadv.abd1211.

Rochman, C.M., Bikker, C.B. Jacqueline, Djuric, Natasha, Earn, Arielle, Bucci, Kennedy, Athey, Samantha, Huntington, Aimee, McIlwraith, Hayley, Munno, Keenan, De Frond, Hannah, Kolomijeca, Anna, Erdle, Lisa, Grbic, Jelena, Bayoumi, Malak, Borrelle, Stephanie B., Wu, Tina, Santoro, Samantha, Werbowski, Larissa M., Zhu, Xia, Giles, Rachel K., Hamilton, Bonnie M., Thaysen, Clara, Kaura, Ashima, Klasios, Natasha, Ead, Lauren, Kim, Joel, Sherlock, Cassandra, Ho, Annissa, Hunga, Charlotte, 2019. Rethinking microplastics as a diverse contaminant suite. Environ. Toxicol. Chem. 38 (4), 703–711. https://doi.org/10.1002/etc.4371.

Rodrigues, M.O., Abrantes, N., Goncalves, F.J.M., Nogueira, H., Marques, J.C., Goncalves, A.M.M., 2018. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antua River, Portugal). Sci. Total Environ. 633, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233.

M.O. Rodrigues, A.M.M. Gonçalves, F.J.M. Gonçalves, N. Abrantes
Improving cost-efficiency for MPs density separation by zinc chloride reuse
Methodsx, 7 (2020), p. 100785, https://doi.org/10.1016/j.mex.2020.100785

M.O. Rodrigues, A.M.M. Gonçalves, F.J.M. Gonçalves, H. Nogueira, J.C. Marques, N. Abrantes
Effectiveness of a methodology of microplastics isolation for environmental monitoring in freshwater systems. Ecol. Indic., 89 (2018), pp. 488-495,
https://doi.org/10.1016/j.ecolind.2018.02.038

Sagawa N., Kawaai K., Hinata H., 2018. Abundance and size of microplastics in a coastal sea: comparison among bottom sediment, beach sediment, and surface water. Mar. Pollut. Bull., 133, pp. 532-542. https://doi.org/10.1016/j.marpolbul.2018.05.036

Sakurada, I., 1985. Polyvinyl alcohol fibers. International Fiber Science and technology Series (Vol. 6). CRC Press. Marcel Dekker, New York and Basel.
Sarkar D.J., Sarkar S.D., Das B.K., Manna R.K., Behera B.K., Samanta S., 2019. Spatial distribution of meso and microplastics in the sediments of river Ganga at eastern India. Sci. Total Environ., 694, p. 133712, https://doi.org/10.1016/j.scitotenv.2019.133712

Scherer C., Weber A., Stock F., Vurusic S., Egerci H., Kochleus C., Arendt N., Foeldi C., Dierkes G., Wagner M., Brennholt N., Reifferscheid G., 2020. Comparative assessment of microplastics in water and sediment of a large European river. Sci. Total Environ., 738, 139866. https://doi.org/10.1016/j.scitotenv.2020.139866

Schneider C., Rasband W., Eliceiri K., 2012. NIH image to ImageJ: 25 years of image analysis Nat. Methods, 9, pp. 671-675. 10.1038/nmeth.2089

Scudo, A.; Liebmann, B., Corden, C.; Tyrer, D.; Kreissig, J.; Warwick, O. Intentionally Added Microplastics in Products, 2017; http://ec.europa.eu/environment/chemicals/reach/ pdf/39168. Intentionally added microplastics - Final report 20171020.pdf. [Accessed on 16th March 2020].

Shumchenia, E. J., Guarinello, M. L. & King, J. W. A re-assessment of Narragansett Bay benthic habitat quality between 1988 and 2008. Estuaries Coasts 39, 1463–1477 (2016). https://doi.org/10.1007/s12237-016-0095-z

Simon-Sánchez L., Grelaud M., Garcia-Orellana J., Ziveri P., 2019. River Deltas as hotspots of microplastic accumulation: the case study of the Ebro River (NW Mediterranean). Sci. Total Environ., 687, pp. 1186-1196, https://doi.org/10.1016/j.scitotenv.2019.06.168

Schmidt, C., Krauth, T., Wagner, S., 2017. Export of plastic debris by rivers into the sea. En- viron Sci Technol 51 (21), 12246–12253. https://doi.org/10.1021/acs.est.7b02368.

Siegfried, M., Koelmans, A.A., Besseling, E., Kroeze, C., 2017. Export of microplastics from land to sea. A modelling approach. Water Res. 127, 249–257. https://doi.org/10.1016/j.watres.2017.10.011.

Sun Y., Yuan J., Zhou T., et al. Laboratory simulation of microplastics weathering and its adsorption behaviors in an aqueous environment: a systematic review[J] Environ. Pollut., 265 (Pt B) (2020), p. 114864. https://doi.org/10.1016/j.envpol.2020.114864

Tibbetts J, Krause S, Lynch I, Sambrook Smith GH. Abundance, Distribution, and Drivers of Microplastic Contamination in Urban River Environments. Water. 2018; 10(11):1597. https://doi.org/10.3390/w10111597

Tien C.-J., Wang Z.-X., Chen C.S., 2020. Microplastics in water, sediment and fish from the Fengshan River system: relationship to aquatic factors and accumulation of polycyclic aromatic hydrocarbons by fish. Environ. Pollut., 265, p. 114962, https://doi.org/10.1016/j.envpol.2020.114962

Tomlinson, D.L., Wilson, J.G., Harris, C.R., Jeffrey, D.W., 1980. Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. Helgoländer Meeresun. 33, 566–575. https://doi.org/10.1007/BF02414780.

UNEP, 2018. Legal Limits on Single-Use Plastics and Microplastics: A Global Review of National Laws and Regulations. United Nations Environment Programme. Available at: https://www.unenvironment.org/resources/report/legal-limits-single-use-plastics- and-microplastics [Accessed on 04 April 2020].

Van Cauwenberghe L., Claessens M., Vandegehuchte M.B., Janssen C.R., 2015. Microplastics are taken up by mussels *(Mytilus edulis)* and lugworms *(Arenicola marina)* living in natural habitats. Environ. Pollut., 199, pp. 10-17. https://doi.org/10.1016/j.envpol.2015.01.008

Wang T., Wang L., Chen Q., Kalogerakis N., Ji R., Ma Y., 2020. Interactions between microplastics and organic pollutants: effects on toxicity, bioaccumulation, degradation, and transport. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2020.142427

Wang J., Peng J., Tan Z., Gao Y., Zhan Z., Chen Q., Cai L., 2017. Microplastics in the surface sediments from the Beijiang River littoral zone: composition, abundance, surface textures and interaction with heavy metals. Chemosphere, 171, pp. 248-258, https://doi.org/10.1016/j.chemosphere.2016.12.074

Wang Z., Su B., Xu X., Di D., Huang H., Mei K., Shang X., 2018. Preferential accumulation of small (<300 μm) microplastics in the sediments of a coastal plain river network in eastern China. Water Res., 144, pp. 393-401. https://doi.org/10.1016/j.watres.2018.07.050

Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine organisms: a review. Environ. Pollut. 178, 483–492. https://doi.org/10.1016/j.envpol.2013.02.031.

Wu P., Tang Y., Dang M., Wang S., Jin H., Liu Y., Jing H., Zheng C., Yi S., Cai Z., 2020. Spatial-temporal distribution of microplastics in surface water and sediments of Maozhou River within Guangdong-Hong Kong-Macao Greater Bay Area. Sci. Total Environ., 717, p. 135187, https://doi.org/10.1016/j.scitotenv.2019.135187

Yang L., Zhang Y., Kang S., Wang Z., Wu C., 2021. Microplastics in freshwater sediment: a review on methods, occurrence, and sources. Sci. Total Environ., 754, p. 141948. https://doi.org/10.1016/j.scitotenv.2020.141948

Yu, F., Yang, C., Zhu, Z., Bai, X., Ma, J., 2019. Adsorption behavior of organic pollutants and metals on micro/nanoplastics in the aquatic environment. Sci. Total Environ. 694, 33643. https://doi.org/10.1016/j.scitotenv.2019.133643.

Zhang Y., Lu J., Wu J., Wang J., Luo Y., 2020. Potential risks of microplastics combined with superbugs: enrichment of antibiotic resistant bacteria on the surface of microplastics in mariculture system. Ecotoxicol. Environ. Saf., 187, p. 109852, https://doi.org/10.1016/j.ecoenv.2019.109852

Zhang L., Liu J., Xie Y., Zhong S., Yang B., Lu D., Zhong Q., 2020. Distribution of microplastics in surface water and sediments of Qin river in Beibu Gulf, China. Sci. Total Environ., 708, p. 135176. https://doi.org/10.1016/j.scitotenv.2019.135176

Zbyszewski M., Corcoran P.L., 2011. Distribution and degradation of freshwater plastic particles along the beaches of Lake Huron, Canada. Water. Air. Soil. Poll., 220 (1–4), pp. 365-372. https://doi.org/10.1007/s11270-011-0760-6

Zbyszewski M., Corcoran P.L., Hockin A., 2014. Comparison of the distribution and degradation of plastic debris along shorelines of the Great Lakes, North America. J. Gt. Lakes. Res., 40 (2) (2014), pp. 288-299. https://doi.org/10.1016/j.jglr.2014.02.012

Ziajahromi S., Kumar A., Neale P.A., Leusch F.D.L, 2017. Impact of microplastic beads and fibers on waterflea (Ceriodaphnia dubia) survival, growth, and reproduction: implications of single and mixture exposures. Environ. Sci. Technol., 51 (22), pp. 13397-13406, https://doi.org/10.1021/acs.est.7b03574

Zhou G., Wang Q., Zhang J., Li Q., Wang Y., Wang M., Huang X. Distribution and characteristics of microplastics in urban waters of seven cities in the Tuojiang River basin, China. Environ. Res. (2020), https://doi.org/10.1016/j.envres.2020.109893

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A. H. M. Enamul Kabir: Conceptualization, Investigation, Methodology, Formal Analysis, Writing– original draft. **Masahiko Sekine:** Supervision, Writing - review & editing. **Tsuyoshi Imai, Koichi Yamamoto, Ariyo Kanno, Takaya Higuchi:** Comments, Writing– Review and Editing

Conflict of Interest

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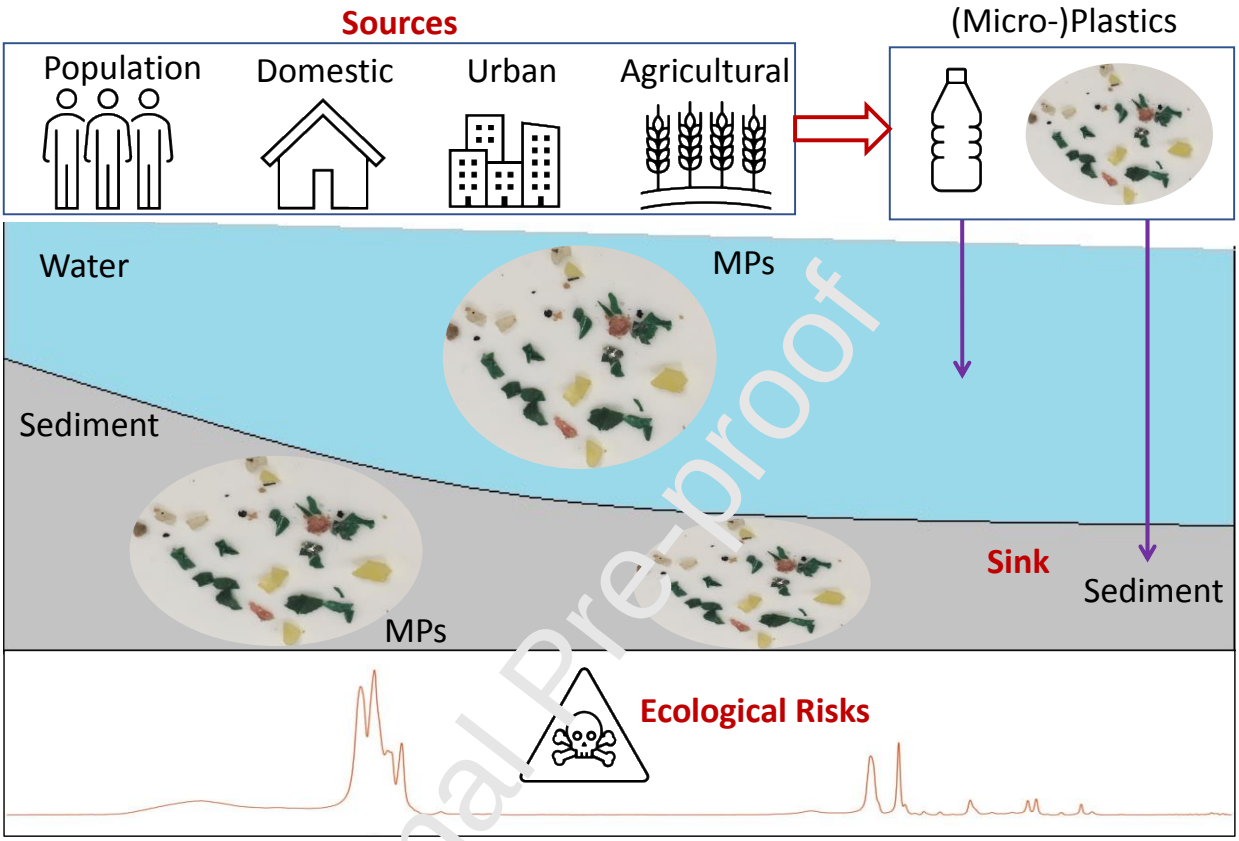
Graphical Abstract



Highlights

- Small-scale riverine sediments were the initial sinks of microplastics
- Large microplastics of high-density polymers were dominant in the sediment
- Microplastics underwent weathering and vectorized metal contaminants
- Urban and highly populated land-use might influence abundance and ecological risks
- Ecological risks were low to high depending on abundances and polymeric toxicity