



Source- and polymer-specific size distributions of fine microplastics in surface water in an urban river^{*}

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ABSTRACT

There is increasing concern about the environmental behaviors of microplastics (MPs), in particular fine MPs (FMPs), such as their concentrations, sources, size distributions, and fragmentation by weathering in waters. However, there is little information about size distributions of MP polymer types and their relationships to their sources. Here, we analyzed concentrations, compositions, and size distributions of 18 polymer types of MPs of $>20 \mu\text{m}$ by micro-Fourier transform infrared spectroscopy with a novel pretreatment method in surface waters at five sites from the headwaters to the mouth of a Japanese river, and in influent and effluent from a sewage treatment plant (STP). The microplastic concentrations ranged from 300 to 1240 particles/m³ in surface waters. Cluster analysis identified two primary sources of MPs: residential wastewater at the headwater site and non-point sources from urban areas at downstream sites; concentrations of chemical contaminants from STPs were much higher at the downstream sites. The median particle sizes (D_{50}) of MPs increased in urban areas at the downstream sites and were larger than those in influent and effluent. These results imply the release of larger MPs from non-point sources in urban areas. The size distributions of each polymer and all MPs could be fitted significantly to the Weibull distribution function. Values of D_{50} , shape parameters, and scale parameters estimated from the functions were useful indicators for evaluating size distributions in detail. A significant positive correlation of D_{50} with the tensile strengths of virgin polymers among 13 dominant polymers detected in the surface water suggests that the fragmentation properties of each polymer are influenced by its physical strength. Multidimensional analysis with concentrations, polymeric compositions, and size distributions of MPs, including FMPs, could provide useful information about their sources and their environmental behaviors.

1. Introduction

The presence of microplastics (MPs) in surface waters is a growing global concern and a major environmental problem. It is estimated that ~ 5.25 trillion pieces of plastic weighing 268 940 t exist in the world's oceans (Eriksen et al., 2014). World plastic production has been increasing dramatically since the 1950s, and was estimated to be 407×10^6 t in 2017 (Geyer et al., 2017). In Europe, 40% of plastic materials are used for packaging, 20% for building and construction, and 10% for automotive manufacture. In Japan, plastic production was $\sim 14.5 \times 10^6$ t in 2016, which had not increased since the 1990s. Plastic marine debris from Japan was also estimated to range from 20 to 60×10^3 t in 2010, ranked 30th in the world (Jambeck et al., 2015). However, there are few reports about the environmental behaviors of MPs in river waters in Japan, although global riverine plastic outflows have drawn great

attention (Mai et al., 2020). In general, wastewater, sewage treatment plant (STP) effluent, and road dust in urban areas are the primary sources of MPs in river waters (Murphy et al., 2016; Gies et al., 2018; Cao et al., 2020; Su et al., 2020; Yukioka et al., 2020). Their occurrence, their characteristics such as size and morphology, and their toxicities in surface waters have been discussed in many previous reports (Baldwin et al., 2016; Anderson et al., 2017; Song et al., 2018; Ding et al., 2019; Lenaker et al., 2019). Some studies estimated the riverine fluxes of large microplastics (LMPs), greater than several hundred micrometers across (Baldwin et al., 2016; Wanger et al., 2019; Constant et al., 2020). However, it was not easy to evaluate their possible sources, their size distributions, or their fragmentation behaviors in waters because observations were limited and had large statistical variability. To reveal the environmental behaviors of MPs from source to sink, monitoring data with higher accuracy and precision based on instrumental analysis,

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without complicated manual operations, is needed, along with data about fine microplastics (FMPs), smaller than several hundred micrometers, and their size distributions (Horton et al., 2017; Akdogan et al., 2019).

Recent field studies conducted to analyze the occurrence of FMPs in surface waters have benefited from micro-Fourier transform infrared spectroscopy (micro-FTIR) or Raman spectroscopy and automated mechanical identification and quantification software (Cabernard et al., 2018; Hendrickson et al., 2018; Corami et al., 2020). These studies suggested that FMPs were present in much higher numbers of particles than LMPs. In addition, the mass of FMPs was estimated to be same order of magnitude as that of LMPs in surface waters in the North Atlantic subtropical gyre with wind-driven vertical mixing (Poulain et al., 2019). Therefore, it will be critical to measure FMPs as well as LMPs in order to estimate their ecological risk and to elucidate their environmental behaviors in surface waters.

Size distributions of MPs are key factors for evaluating ecological and human health risks and the formation of MPs from plastic products in the environment. Recent reports have presented size distributions of MPs in surface waters or STP effluent (Enders et al., 2015; Park et al., 2020). Some show that size distributions of MPs and nano-plastics generated intentionally from different polymer types and different forms of plastics can be expressed by mathematical functions (Lambert et al., 2016; Astner et al., 2019). The functions could also indicate particle size distributions among polymer types and differences in degradation conditions. But they could not elucidate size distributions clearly because of the high variability of MP particle populations. There is little information about the size distributions of polymers in surface waters in association with their material properties such as physical strength, though it is easy to predict that size distributions will be influenced by physico-chemical properties and weathering processes. In general, many previous reports presented size distributions of MPs in surface waters or sediments as discrete bins. As the result, they cannot reveal their properties clearly and quantitatively because of analytical errors and high variability (Klein et al., 2015; Mao et al., 2020.).

In these cases, it is useful to fit observed data to numerical formulas and evaluate properties of size distributions from several parameters. Actually, recent studies have proposed numerical formulas that can express size distributions of MPs in wastewater and environmental samples (Kooi et al., 2019; Park et al., 2020).

Here, we investigated the abundance, polymer compositions, and size distributions of FMPs and LMPs (20 µm–5 mm) in river surface water samples collected from the headwaters to the river mouth by an on-site collecting method, using novel techniques based on micro-FTIR. The Weibull distribution function was used to characterize the size distributions of MPs and each plastic polymer. From these data, sources of MPs in the water, fragmentation properties of MPs from their sources to the river mouth, and source- and polymer-specific size distributions were revealed.

2. Materials and methods

2.1. Sampling area

Samples were collected under base flow conditions in August 2018 at five sites on the main stream of the Tsurumi River, Japan (Fig. 1, S1; Table S1), from the headwaters to the river mouth. The catchment drainage area is 235 km²; ~2 million people live in the catchment. Because the basin has a variety of land cover along the river, water qualities vary among the sites. Site A was a stream of groundwater drawn in a small village at the top of a mountain; 82.4% of its catchment is covered with forests and fields. Site B was located in an urban residential area, home to 53 000 residents. However, there are no STPs in the catchment. Therefore, the wastewater, which is treated in household septic tanks, flows through pipes into the river. Urban runoff from the catchment also flows directly into the river. Therefore, the annual

average concentration of biological oxygen demand (BOD) at Site B is 4.7 mg/L, according to local government information. At Site C, the flow rate is remarkably higher than at Sites A and B, because 0.73 m³/s of effluent is released into the river from two small STPs, which treat wastewater loads of ~123 000 and ~161 000 persons, respectively. There are also many small tributaries between Sites B and C, which jointly add is 2.95 m³/s to the main stream. The BOD at Site C is 2.0 mg/L, less than that at Site B because of dilution by clear surface water from the small tributaries. There are three large STPs between Sites C and D, which purify wastewater from three metropolitan areas in which 244 000, 514 000, and 616 000 people live. The treated water from these STPs increases contamination at Site D, where the BOD is 2.7 mg/L. Site E has various potential sources of contamination because it is located near residential and industrial areas at the river mouth. Effluent from two other STPs, which treat wastewater loads of 300 000 and 331 000 persons, also enters between Sites D and E. The surface waters at Sites D and E are influenced by pollutants originating from Tokyo Bay because of the influx of seawater. In total, there are seven STPs along the Tsurumi River, and the area downstream of Sites D and E is one of the largest metropolitan areas in Japan.

2.2. Sample processing

At each site we collected ~1 m³ of river water from 10 to 20 cm beneath the surface near the center of the river (Fig. S2) in a 20-L polyethylene tank and then measured the volume. Then the water was passed through the plankton nets with a 10-µm mesh size by small electric pumps set up on the river bank (Fig. S1). The nets were then washed with ~2 L of tap water in the laboratory to wash off MPs, organic debris, and other suspended solids. The MP content in tap water was negligible, as described in detail in section 2.5. The solids and washing water were transferred into a glass bottle and stored in a refrigerator before analysis.

At an STP with a separate sewer system in the catchment of the Tsurumi River, we collected 1 L of influent and 10 L of effluent. The influent sample was collected in steel buckets from the primary settling tank and stored in a glass bottle. The sample was taken to our laboratory and passed through the plankton nets. The effluent sample was collected at the outfall from the STP and was passed through the nets on site.

We also collected 1 L of river surface water at each site to measure ingredients of personal care products (PCPs) in order to estimate the contributions of residential wastewater and effluent from STPs to surface waters. Each sample was collected in a glass bottle washed with acetone, taken to our laboratory, and stored in a refrigerator before analysis.

2.3. Isolation of microplastics from surface water, influent, and effluent samples

It is important for analysis of MPs to reduce contamination and recover enough plastic particles. We established a pretreatment process without separatory funnels for MPs of >20 µm (Fig. S3). Particulate matter collected on the plankton nets from all samples was collected on several hydrophilic PTFE filter membranes (Merck Millipore, Darmstadt, Germany) with a pore size of 5.0 µm. The membranes were pooled in a tall-form 200-mL beaker and 40 mL of 30% hydrogen peroxide was added slowly for digestion of organic matrices at 60 °C for a few days with stirring at 100 rpm under a glass lid. After digestion was judged sufficient, ultra-purified water was added up to 100 mL, and finally 100 g of sodium iodide was added into the beaker. After stirring for 10 min, the solution was stored statically for >6 h for density separation. The specific gravity of the solution was 1.7. Then 20 mL of supernatant was transferred in a small ladle from the beaker into another beaker. The stirring and supernatant collection procedure was repeated three times and the supernatants were pooled in the beaker. Finally, 60 mL of the supernatant was passed through an area of 18 mm diameter in a 47-mm-

diameter hydrophilic PTFE membrane in a thin glass filter holder (Advantec, Tokyo, Japan) to accumulate MPs on the membrane (Fig. S4). The membrane was then immediately fixed on a purpose-designed plate to prevent rolling during drying.

2.4. Identification and quantification of MPs

Microplastics collected on the membrane were identified by infrared (IR) microscopy without manual picking of potential particles. The dried membrane was directly mounted on the stage of a Nicolet iN 10MX FTIR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to a microscope. The IR absorption spectra of three regions of the membrane (center, upper edge, and right edge) were measured in transmission mode. The spectral range was set at 4000–650 cm⁻¹ with a spectral resolution of 4 cm⁻¹. Each scan area was 25 mm², and their total corresponded to 29.4% of the whole filtration area (Fig. S5). IR spectra were collected by scanning the mechanically controlled microscope stage in increments of 15 µm with a 30-µm × 30-µm rectangular field aperture. Therefore, the whole IR spectrum was obtained in each pixel with a size of 15 µm × 15 µm. The scanning areas were overlaid on each other because measurement with a larger aperture in layers can better detect weak IR absorption spectra of MP particles of 20 µm than non-overlapping scanning. The spectral background was measured on the PTFE membrane. For each scan area, ~110 000 whole IR spectral data were collected and mapped as an IR hyperspectral image at high resolution in OMNIC Picta software (Thermo Fisher Scientific Inc.). We identified and quantified 18 polymer types: acrylonitrile-butadiene-styrene (ABS), Alkyd resin (Alkyd), styrene-acrylonitrile resin (AS), epoxy resin (Epoxy), styrene-butadiene (SBR), polyethylene (PE), poly(ethyleneterephthalate) (PET), polyisoprene (PIP), poly(methylmethacrylate) (PMMA), polyamide (PA), polypropylene (PP), polystyrene (PS), poly(phenylene sulfide) (PPS), polyurethane foam (PU), poly(vinylacetate) (PVAc), poly(vinylalcohol) (PVAL), poly(vinylchloride) (PVC), and poly(vinylmethylether) (PVME) (Table S2). We categorized particles identified as acrylic resin as PMMA and mixtures of PE and PP as PE. Two reference spectra libraries were used to identify polymer types. One stores fresh plastic polymers in OMNIC Picta software (e.g., HR Hummel Polymer and Additives, HR Sprouse Polymers by Transmission, HR Condensed Phase Academic Sampler, HR Aldrich FT-IR Collection Edition II, HR Toronto Forensic, HR Polymer Additives and Plasticizers, and Aldrich polymers). The other is an original library which includes environmentally relevant polymers observed in this study. To identify and quantify all polymer types from the IR hyperspectral image, we generated 18 new polymer-specific chemical images for each polymer type in OMNIC Picta by calculating the matching score in each pixel from correlation analysis between the observed IR spectrum and the reference library spectrum. Particles, fibers, and fragments of each polymer type with matching scores of >60% were extracted as candidate MPs in each image. However, some of them, especially MPs of ~≤20 µm, seemed to be misidentified. Therefore, final identifications used all polymer-specific bands, mostly 5 to 15 peaks per spectrum. Identifications were considered complete when all polymer-specific bands were observed from the spectra of candidate MPs. The final MPs were counted by polymer in OMNIC Picta scanning software, which also measured their minor and major axes. Fibrous MPs were defined when the major axis was ≥3 times the minor axis. Concentrations of MPs were described as their mean and standard deviation calculated from the particle counts of MPs in three scan areas, because counts of some polymers seemed to be heterogeneous on the membrane, especially in samples at upstream sites (Table S3).

2.5. Quality assurance and quality control

Laboratory experiments were conducted in a clean room by analysts dressed white cotton clothes. Glass beakers and all other apparatus for MP analysis were stored on a clean metal shelf before experiments.

Sample filtration used several liters of tap water, which might have contaminated the samples, but the contamination would be negligible, because MP concentrations in the tap water were measured at only 0.2 to 0.3 particles/L (<1 particle per sample). We did not test contamination from the air, NaI reagent, or analytical operations independently, but we tested for contamination in all processes during sampling, isolation, and micro-FTIR analysis. We analyzed 1 m³ of tap water filtered through a 0.45-µm PTFE membrane in triplicate and detected only PE and PP at a total of only 7.6 ± 2.5 particles/m³ (mean ± SD). The number of MPs counted in three square scan areas (75 mm²) on the membrane ranged from 88 to 365 particles in all samples, much higher than in the blanks (2.2 ± 0.74 particles/75 mm²).

To determine rates of MP recovery in the isolation procedure, we analyzed twenty 1-L lots of water containing 100 particles of commercial polyethylene beads (32–38 µm; Cospheric LLC, Santa Barbara, CA, USA) as above. One hundred particles were placed on a plate from the reagent bottle by using a thin needle under microscopic observation and were added to tap water filtered through a 0.45-µm PTFE membrane. The added particles were isolated as described in section 2.3. Recovery rates ranged from 94% to 100%.

2.6. Chemicals and analytical methods for PCPs

In order to estimate a contribution of wastewater or effluent from the STP to total river water, we analyzed 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8,-hexamethyl-cyclopenta[g]benzopyran (HHCB), 6-acetyl-1,1,2,4,4,7-hexamethyltetraline (AHTN), caffeine, and crotamiton in surface water samples by a revised method of Nakada et al. (2008). Standard chemicals of PCPs were purchased from Dr Ehrenstorfer GmbH, Ausburg, Germany, except caffeine (LKT Laboratories, Inc., St. Paul, MN, USA) and crotamiton (Fujifilm Wako Chemical Corporation, Osaka, Japan). Caffeine-d9 and musk xylene-d9 were purchased from Toronto Research Chemicals, Inc. (Toronto, ON, Canada). In brief, 1 L of surface water samples fortified with caffeine-d9 and musk xylene-d9 was passed through an SPE cartridge (Oasis HLB, 6 cc, 200 mg; Waters Corporation, Milford, MA, USA) at 10 mL/min. PCPs were eluted with 10 mL of methanol. The extracts were evaporated close to dryness under a nitrogen gas stream and then analyzed in single-ion monitoring mode by gas chromatography – mass spectrometry (QP-2010, Shimadzu Corp., Kyoto, Japan). Rates of recovery in triplicate tests using ultrapure water were 75.9% ± 5.0% HHCB, 89.4% ± 2.3% AHTN, 89.3% ± 1.9% caffeine, and 71.6% ± 1.8% crotamiton.

2.7. Data analysis

Hierarchical cluster analysis was performed in JMP software (v. 5.0.1a; SAS Institute Inc., Cary, NC, 1989–2002). Ratios of each polymer concentration to total MP concentration were normalized. Cluster analysis was conducted using Ward's method to show proximity among concentration profiles of polymers at all sampling sites.

The major axis of particles was used to reveal the size distributions of MPs in all samples. The size distributions were fitted to the two-parameter Weibull distribution model as follows:

$$p = 1 - \exp\{- (d/a)^\beta\} \quad (1)$$

where p is the MP cumulative ratio, d is major axis of MP particles, α is the scale parameter, and β is the shape parameter of the distribution. Equation (1) was fitted by non-linear regression to estimate α and β for all MPs and major plastic polymers at each site. Minor polymers (<5 observed particles) were not analyzed. Non-linear regression analysis was performed using the Solver optimization tool of Microsoft Excel as recommended by Brown (2001) and Prata et al. (2016). Curve-fitting performance was evaluated by unweighted least squares criterion, the coefficient of determination (R^2) and visual inspection. The 10th (D_{10}), 50th (median, D_{50}), and 90th (D_{90}) size of the distributions were

calculated from the estimated models.

3. Results and discussion

3.1. Occurrence of FMPs in samples in relation to chemical pollutants

Fig. 2 shows the MP concentrations and their polymer compositions in surface water, influent, and effluent samples and the chemical pollutants in the Tsurumi River (detailed concentration data in **Table S3**). Site A was the least contaminated among the five sites: the concentrations of all chemical pollutants were $<0.2 \mu\text{g/L}$ and the BOD concentration was 0.7 mg/L (**Table S1**). Though the chemical pollutant concentrations at Site B were of the same order of magnitude as those at Site A, the BOD concentration was remarkably higher than at Site A. This difference implies that other contaminants from residential wastewater were released from the catchment. A possible origin was nonpoint sources in the catchment, because urban areas are much larger in the catchment of Site B than of Site A (**Table S1**). On the other hand, the ratios of caffeine to crotamiton concentrations were $\gg 1$, but those at the downstream sites were <1 , indicating that Sites C, D and E were contaminated by the large volumes of treated wastewater from STPs along the river (Nakada et al., 2008). The results also agree with the increase of HHCB and AHTN concentrations. Therefore, one of the major contamination sources at Sites C to E was STP effluent according to chemical pollutants compositions. A remarkable decrease in the concentrations of synthetic fragrances at Site E due to dilution by seawater suggested that seawater also influences water quality at Site E (**Fig. 2**).

Concentrations of MPs ranged from $298 \pm 105 \text{ particles/m}^3$ to $1240 \pm 295 \text{ particles/m}^3$ at all sampling sites, and were $1030 \pm 212 \times 10^3 \text{ particles/m}^3$ in influent and $2370 \pm 513 \text{ particles/m}^3$ in effluent. The concentrations were much higher than those in previous studies of river surface water in Japan and other countries because mesh size in this study was much smaller ($10 \mu\text{m}$) than previous studies (Kataoka et al., 2019; Horton et al., 2017). For example, Kataoka et al. (2019) reported a concentration of $4.85 \text{ particles/m}^3$ based on $335\text{-}\mu\text{m}$ -mesh plankton nets near Site D, but we found $884 \text{ particles/m}^3$, which indicates that the concentration of FMPs was approximately 200 times that of LMPs. However, we observed $109 \text{ particles/m}^3$ of MPs $>335 \mu\text{m}$, which corresponds to 12.3% of all MPs. One reason is considered to be precise identification by micro-FTIR, which can detect all MPs, even clear or film-type ones overlooked frequently. It is suggested that smaller MPs could have adverse effects which are different from the effects of larger MPs on aquatic organisms (Deng et al., 2017), although there is little information about their concentrations and size distributions. Therefore, it is important to measure FMPs with both high accuracy and high precision in order to reveal total MP concentrations, their potential sources, and their environmental behaviors in waters.

Ten to fourteen types of polymers were detected in surface water samples. Seven were detected at all sampling sites, namely Alkyd, AS, PE, PMMA, PP, PS, and PVC. The most predominant polymers were PE and PP, in agreement with previous reports of LMPs in surface waters in the USA, France, and China (Lenaker et al., 2019; Li et al., 2019; Constant et al., 2020). The contribution of the 7 polymers ranged from $267 \text{ particles/m}^3$ to $1050 \text{ particles/m}^3$, which corresponded to 82.7–97.7% of the total MP concentration at all sampling sites. Four polymers were not detected at any sites: PIP, PPS, PVAI, and PVME. Concentrations of MPs in STP influent and effluent were higher than those in previous reports of LMPs in Canada, China, Finland, France, Korea, the Netherlands, Scotland, Sweden and the USA because we used finer plankton nets ($10 \mu\text{m}$) than in the previous reports (Park et al., 2020). However, Alkyd, PE, PET, PMMA, and PP were the dominant polymers among FMPs in this study, in good agreement with polymer compositions in previous reports of LMPs. These results indicate that these would be key polymers to assay for in surface water samples and STP samples in order to reveal the occurrence and environmental behaviors of FMPs in aquatic environments.

Ten polymer types of fibrous MPs were detected in surface water samples (**Fig. S6**), at $23.7 \text{ particles/m}^3$ to $122 \text{ particles/m}^3$, which corresponded to 9.9%–5.4% of the concentrations of all MPs at each site. Only 6 polymers were detected in the STP influent and effluent (**Fig. S7**). Large numbers of fibrous PET MPs are released from clothes during washing (Cai et al., 2020; Fontana et al., 2020; Hernandez et al., 2017). We also found prominent amounts of fibrous PET MPs in the STP influent and effluent, but fibrous Alkyd and PP MPs were also predominant in the surface water. Polypropylene fibers are used in much clothing in Japan, and some could be released during washing. Alkyd-resins are generally used in road-marking paints on a massive scale in Japan. Some of them could be released into rivers via transfer by wind and runoff from urban areas after peeling off. But further research is needed to find potential sources of fibrous Alkyd MPs and mechanisms of their generation.

3.2. Size distributions of MPs from the headwaters to the river mouth

The observed size distribution of all MPs in the samples could be fitted to the Weibull distribution function (**Table S4**). All regression coefficients ranged from 0.81 to 1.0. Previous reports expressed size distributions of MPs generated from plastic materials or STP influent and effluent by a gamma distribution or a power law distribution (Lambert et al., 2016; Park et al., 2020). The size distributions of MPs in STP influent and effluent appeared finer than those in surface water samples (**Fig. 3**). D_{50} values of both STP influent and effluent, at $39 \mu\text{m}$ and $42 \mu\text{m}$ respectively, were much smaller than those of surface water samples, at 64 – $131 \mu\text{m}$. The scale parameters (α) of cumulative distribution

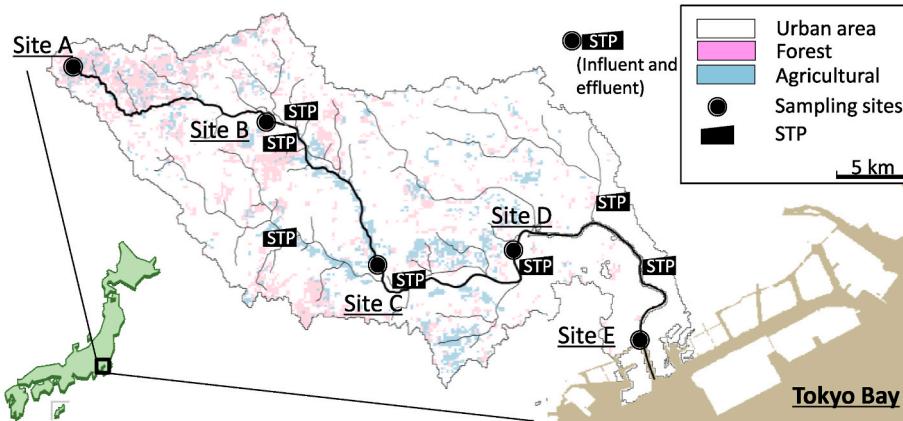


Fig. 1. Sampling sites, sewage treatment plants, and land use along the Tsurumi River, Japan.

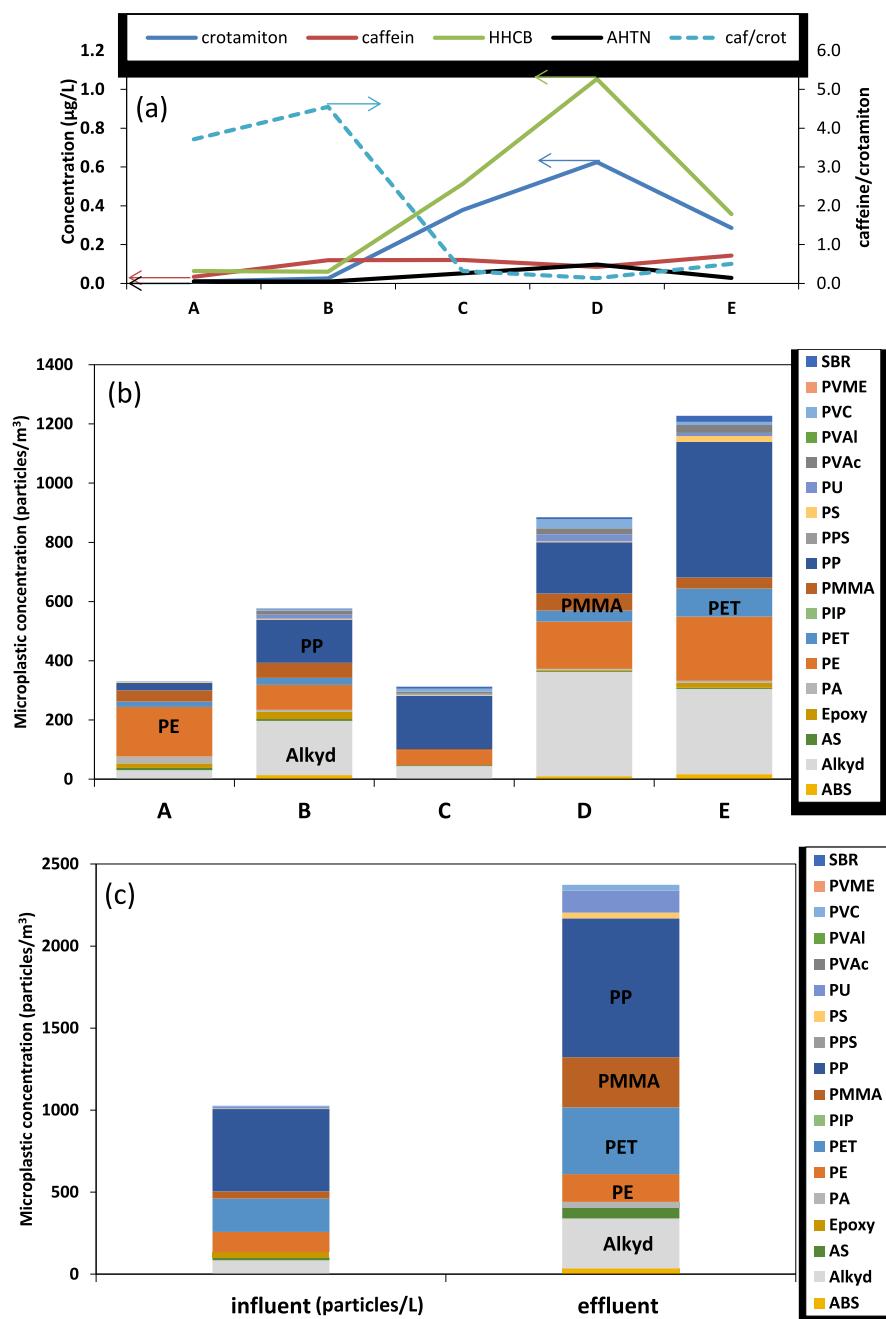


Fig. 2. Concentrations of chemical contaminants (a) and polymer types of MPs (b) in surface water along the river as well as microplastic concentrations in STP samples (c).

functions also indicate that surface water samples were much larger than those of influent and effluent (Fig. S8). The results suggest that the distributions of the surface water samples had larger variance than those of the influent and effluent. They also imply that large and heterogeneous sizes of MPs were derived from other sources than residential wastewater and STP effluent. On the other hand, values of the shape parameter (β) of the distribution functions of MP polymers ranged from 0.7 to 5.9, and most values of all polymers at downstream sites were around 1.0, smaller than those of STP samples (2.0–5.9). Generally, the distributions are two-parameter exponential functions when $\beta = 1$ and are close to normal distribution functions when β values increase to 3.6. These results suggest that distribution functions of polymers followed normal distributions of finere particles in STP samples and exponential distributions of coarser particles at the downstream sites. Thus, D_{50} , shape parameters, and scale parameters from the Weibull distribution

function of MPs are useful indicators for evaluating properties of MP distributions in aquatic environments. However, further investigation of functions which can better reveal size distributions is needed.

3.3. Classification of polymer compositions in surface water by cluster analysis plus MP size distributions

Previous reports used multivariate analysis to compare the characteristics of microplastics between dry and wet seasons or among sampling sites (Jiang et al., 2020; Su et al., 2020; Zayen et al., 2020; Wang et al., 2021). These reports indicated that principal component analysis highlighted size class, shape, and color of LMPs as relevant and clearly demonstrated the closeness of MPs profiles at each sampling site and season. However, a lack of polymer information made it difficult to estimate their potential sources. Fig. 4 shows hierarchical cluster analysis

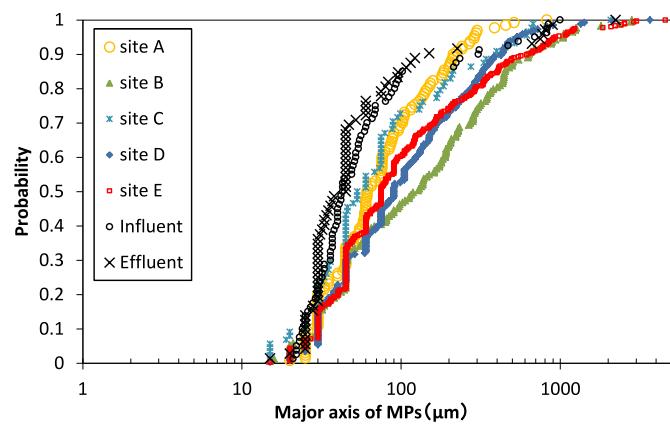


Fig. 3. Observed cumulative size distributions of all MPs collected from five sampling sites and in STP influent and effluent.

based on concentrations of MPs of 18 polymer types at all sites. The cluster analysis revealed two major groups, one related to residential wastewater (Group 1), the other to downstream sites (Group 2). Group 1 was considered “wastewater type” because of wastewater effluent and land use at site A (a small village surrounded by forests and fields with no STP). Group 2 was considered to be influenced by unknown sources which were different from wastewater. Group 2 was sub-classified into Sites B + D (Group 3) and Sites C + E (Group 4). These 4 groups were very similar to the classification of the D_{50} values of MPs at each site in Fig. 3, which placed site A and the STP influent and effluent (small MPs) in Group 1, the other sampling sites (larger MPs) in Group 2, Site B + D (largest D_{50}) in Group 3 and Site C + E (smaller D_{50}) in Group 4, although the MP size data were not used in the cluster analysis. This coincidence of results from 2 different analytical methods suggests that Group 2 was more contaminated by MPs from nonpoint sources in urban areas than by those in wastewater, and that the size distribution and polymer composition of MPs depend strongly on their sources. For example, a high portion of MPs in road surface dust ranged in size from 300 to 1400 μm and comprised rubber MPs such as PU and SBR and container or packing MPs (Yukioka et al., 2020). We also found SBR, PU, and ABS only at downstream sites, and their D_{50} and many scale parameters of the estimated Weibull distribution functions ranged from 55 to 154 μm and from 85.3 to 211 μm , respectively. These values were relatively larger than D_{50} (71 μm) and scale parameters (91.5) of all MPs at Site A (Tables S3, S4). From these results, we presume that size distributions of MPs in river surface water could be strongly influenced by polymer compositions and sources of MPs.

3.4. Factors involved in the discrepancy among particle sizes of each polymer type in surface waters

Large plastic products or debris are likely to be fragmented in the environment by weathering due to photodegradation, photothermal

oxidation, hydrolysis, biodegradation, or mechanical abrasion (Cai et al., 2018; Song et al., 2017; Andray, 2017). Because different polymers respond uniquely to each of these processes, it is hard to evaluate size distributions of all MPs in surface water as well as their fragmentation properties. In fact, the scale parameters of the size distribution functions of PMMA and PP were significantly different from those of PET in surface water samples (Fig. S9). Some reports evaluated degradation properties of some polymers from their tensile strengths (Arhant et al., 2019; Guen-Geffroy et al., 2019). We compared the size distributions (D_{50}) of the 13 dominant polymers at each sampling site with their tensile strengths of virgin polymers (Fig. 5) and found a statistically significant positive correlation: polymers with higher tensile strengths had larger D_{50} values. D_{50} values of PE and PP, with low tensile strengths, were <100 μm , similar to those from fragmentation experiments with PE, PP, and expanded polystyrene under UV exposure and mechanical abrasion (Song, 2017). D_{50} values of PET, ABS, and Alkyd, with high tensile strengths, were large, because fibrous MPs were more common in PET and Alkyd than in other polymers. We consider that these polymers with high tensile strengths might be difficult to fragment by weathering during their short transfer from catchment to river in this investigation. Further researches about this relation are needed especially for MPs in oceans. Thus, tensile strengths of virgin polymers, as

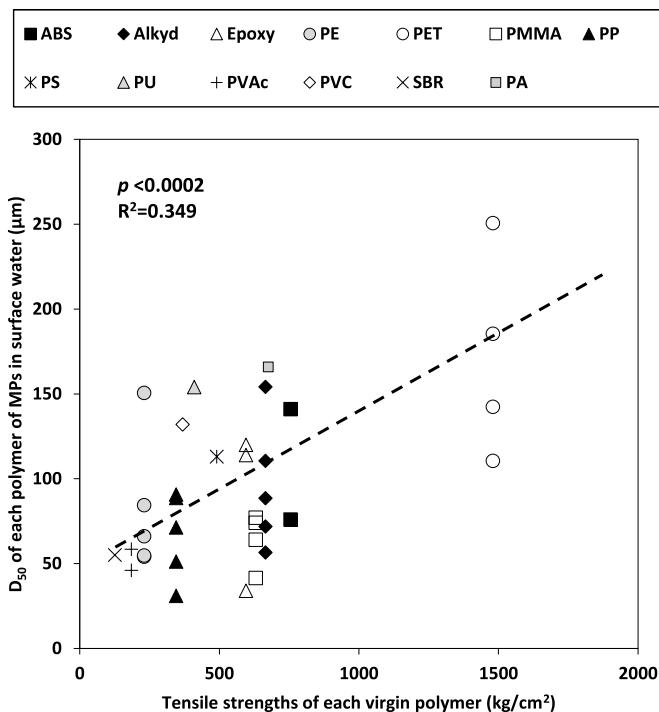


Fig. 5. Relationship between tensile strengths of virgin materials and D_{50} of 13 plastic polymers in river.

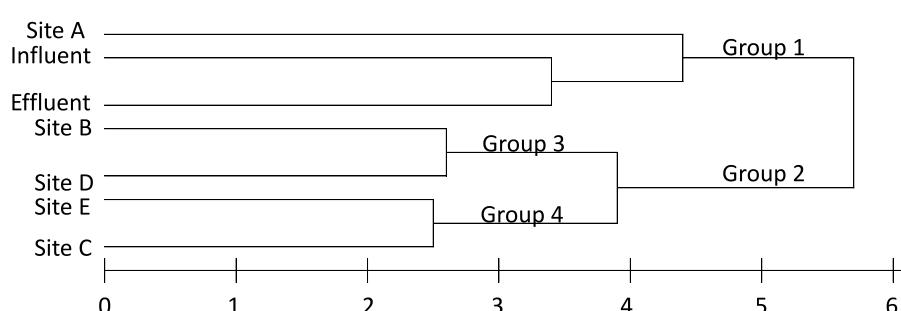


Fig. 4. Cluster analysis of the polymer compositions in surface water at all sampling sites.

well as sources and polymer types, can influence size distributions of MPs in river water.

4. Conclusion

This study shows detailed analysis of concentrations, polymeric compositions, and size distributions of 18 polymer types of MPs (20 µm–5 mm) in urban surface water contaminated by wastewater, STP effluent, and nonpoint sources from urban areas. Concentrations of MPs were higher at downstream sites; the highest was 1240 particles/m³, at the river mouth. D₅₀ values of size distributions of MPs increased at the downstream and were larger than those in STP influent and effluent. This result clearly indicates that more LMPs were released to the river from various nonpoint sources in the catchment than from residential wastewater and STP effluent. On the other hand, hierarchical cluster analysis based on the polymeric compositions of MPs estimated two predominant profiles of MPs—residential wastewater type, observed in the headwaters, and nonpoint-source type at the urbanized downstream sites, composed of polymers unique to urban areas, such as SBR, PU, and ABS. Observed polymer-specific size distributions in the surface water could also be evaluated by two parameters of the Weibull distribution function. The median sizes, D₅₀, had a significant relation with tensile strengths of virgin polymers. These results show that multidimensional analysis based on concentration, polymeric composition, and size distribution of MPs with the Weibull distribution function is a powerful tool for estimating sources and environmental behaviors of plastics. Further research on MPs of <20 µm should be conducted to reveal occurrences, size distributions, and environmental behaviors of all MPs.

Author statement

Yutaka Kameda: Conceptualization, Methodology, Validation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition, Supervision. Naofumi Yamada: Methodology, Validation, Investigation. Emiko Fujita: Methodology, Validation, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2021.117516>.

References

- Akdogan, Z., Guven, B., 2019. Microplastics in the environment: a critical review of current understanding and identification of future research needs. *Environ. Pollut.* 254, 113011.
- Anderson, P.J., Warrack, S., Langen, V., Challis, J.K., Hanson, M.L., Rennie, M.D., 2017. Microplastic contamination in lake winnipeg, Canada. *Environ. Pollut.* 225, 223–231.
- Andrade, A., 2017. The plastic in microplastics: a review. *Mar. Pollut. Bull.* 119, 12–22.
- Arhant, M., Gall, M.L., Gac, P.-Y.L., Davies, P., 2019. Impact of hydrolytic degradation on mechanical properties of PET-Towards an understanding of microplastics formation. *Polym. Degrad. Stabil.* 161, 175–182.
- Astner, A.F., Hayes, D.G., O'Neill, H., Evans, B.R., Pingali, S.V., Urban, V.S., Young, T.M., 2019. Mechanical formation of micro- and nano-plastic materials for environmental studies in agricultural ecosystems. *Sci. Total Environ.* 685, 1097–1106.
- Baldwin, A.K., Corsi, S.R., Mason, S.A., 2016. Plastic debris in 29 great lakes tributaries: relation to watershed attributes and hydrology. *Environ. Sci. Technol.* 50, 10377–10385.
- Brown, A.M., 2011. A step-by-step guide to non-linear regression analysis of experimental data using a Microsoft Excel spreadsheet. *Comput. Methods Programs Biomed.* 65, 191–200.
- Cabernard, L., Roscher, L., Lorenz, C., Gerdzt, G., Primpke, S., 2018. Comparison of Raman and Fourier transform infrared spectroscopy for the quantification of microplastics in the aquatic environment. *Environ. Sci. Technol.* 52, 13279–13288.
- Cai, Y., Yang, T., Mitrano, D.M., Heuberger, M., Hufenus, R., Nowack, B., 2020. Systematic study of microplastic fiber release from 12 different polyester textiles during washing. *Environ. Sci. Technol.* 54, 4847–4855.
- Cai, L., Wang, J., Peng, J., Wu, Z., Tan, X., 2018. Observation of the degradation of three types of plastic pellets exposed to UV radiation in three different environments. *Sci. Total Environ.* 628, 740–747.
- Cao, Y., Wang, Q., Ruan, Y., Wu, R., Chen, L., Zhang, K., Lam, P.K.S., 2020. Intra-day microplastic variations in wastewater: a case study of a sewage treatment plant in Hong Kong. *Mar. Pollut. Bull.* 160, 111535.
- Constant, M., Ludwig, W., Kerhervé, P., Sola, J., Charrière, B., Sanchez-Vidal, A., Canals, M., Heussner, S., 2020. Microplastic fluxes in a large and a small Mediterranean river catchments: the Têt and the Rhône, northwestern Mediterranean Sea. *Sci. Total Environ.* 716, 136984.
- Corami, F., Rosso, B., Bravo, B., Gambaro, A., Barbante, C., 2020. A novel method for purification, quantitative analysis and characterization of microplastic fibers using Mirco-FTIR. *Chemosphere* 238, 124564–124573.
- Ding, J., Jiang, F., Li, J., Wang, Z., Sun, C., Wang, Z., Fu, L., Ding, N.X., He, C., 2019. Microplastics in the coral reef systems from Xisha islands of south China Sea. *Environ. Sci. Technol.* 53, 8036–8046.
- Deng, Y., Zhang, Y., Lemos, B., Ren, H., 2017. Tissue accumulation of microplastics in mice and biomarker responses suggest widespread health risks of exposure. *Sci. Rep.* 7, 46687.
- Enders, K., Lenz, R., Stedmon, C.A., Nielsen, T.G., 2015. Abundance, size and polymer composition of marine microplastics ≥10 µm in the Atlantic Ocean and their modelled vertical distribution. *Mar. Pollut. Bull.* 100, 70–81.
- Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.L., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PloS One* 9, e111913.
- Fontana, G.D., Mossotti, R., Montarsolo, A., 2020. Assessment of microplastics release from polyester fabrics: the impact of different washing conditions. *Environ. Pollut.* 264, 113960.
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Science Advances* 3, e1700782.
- Gies, E.A., Lenoble, J.I., Noel, M., Etemadifar, A., Bishay, F., Hall, E.R., Ross, P.S., 2018. Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. *Mar. Pollut. Bull.* 133, 553–561.
- Guen-Geffroy, A.L., Gac, P.-Y.L., Habert, B., Davies, P., 2019. Physical ageing of epoxy in a wet environment: coupling between plasticization and physical ageing. *Polym. Degrad. Stabil.* 168, 108947.
- Hendrickson, E., Minor, E.C., Shreiner, K., 2018. Microplastic abundance and composition in western Lake Superior as determined via microscopy, Pyr-GC/MS, and FTIR. *Environ. Sci. Technol.* 52, 1787–1796.
- 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, 7036–7046.
- Horton, A., Walton, A., Spurgeon, D., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: valuating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ.* 586, 127–141.
- 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.
- Jiang, Y., Yang, F., Zhao, Y., Wang, J., 2020. Greenland Sea Gyre increases microplastic pollution in the surface waters of the Nordic Seas. *Sci. Total Environ.* 712, 136484.
- 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.
- 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, 6070–6076.
- Kool, M., Kolemans, A.A., 2019. Simplifying microplastic via continuous probability distributions for size, shape and density. *Environ. Sci. Technol. Lett.* 6, 551–557.
- Lambert, S., Wagner, M., 2016. Formation of microscopic particles during the degradation of different polymers. *Chemosphere* 161, 510–517.
- Lenaker, P.L., Baldwin, A.K., Corsi, S.R., Mason, S.A., Reneau, P.C., Scott, J.W., 2019. Vertical distribution of microplastics in the water column and surficial sediment from the Milwaukee river basin to Lake Michigan. *Environ. Sci. Technol.* 53, 12227–12237.
- Li, L., Geng, S., Wu, C., Song, K., Sun, F., Visvanathan, C., Xie, F., Wang, Q., 2019. Microplastics contamination in different trophic state lakes along the middle and lower reaches of Yangtze River basin. *Environ. Pollut.* 254, 112951.

- Mao, Y., Li, H., Gu, W., Yang, G., Liu, Y., He, Q., 2020. Distribution and characteristics of microplastics in the Yulin River, China: role of environmental and spatial factors. *Environ. Pollut.* 265, 115033.
- Mai, L., Sun, X.F., Xia, L.L., Bao, L.J., Liu, L.Y., Zeng, E.Y., 2020. Global riverine plastic outflows. *Environ. Sci. Technol.* 54, 10049–10056.
- 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, 5800–5808.
- Nakada, N., Kiri, K., Shinohara, H., Harada, A., Kuroda, K., Takizawa, S., Takada, H., 2008. Evaluation of pharmaceuticals and personal care products as water-soluble molecular markers of sewage. *Environ. Sci. Technol.* 42, 6347–6353.
- Park, H.J., Oh, M.J., Kim, P.G., Kim, G., Jeong, D.H., Ju, B.K., Lee, W.S., Chung, H.M., Kang, H.J., Kwon, J.H., 2020. National reconnaissance survey of microplastics in municipal wastewater treatment plants in Korea. *Environ. Sci. Technol.* 54, 1503–1512.
- Poulain, M., Mercier, M.J.R., Brach, L., Martignac, M., Routaboul, C., Perez, E., Desjean, M.C., Halle, A., 2019. Small microplastics as a main contributor to plastic mass balance in the north Atlantic subtropical gyre. *Environ. Sci. Technol.* 53, 1157–1164.
- Prata, J.R.A.A., Santos, J.M., Beghi, S.P., Fernandes, I.F., Vom Marttens, L.L.C., Pereira Neto, L.I., Martins, R.S., Reis, J.R.N.C., Stuetz, R.M., 2016. Dynamic flux chamber measurements of hydrogen sulfide emission rate from a quiescent surface – a computational evaluation. *Chemosphere* 146, 426–434.
- Song, Y.K., Hong, S.H., Eo, S., Jang, M., Han, G.M., Isobe, H., Shim, W.J., 2018. Horizontal and vertical distribution of microplastics in Korean Coastal waters. *Environ. Sci. Technol.* 52, 12188–12197.
- Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Jung, S.W., Shim, W.J., 2017. Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. *Environ. Sci. Technol.* 51, 4368–4376.
- Su, L., Nan, B., Craig, N.J., Pettigrove, V., 2020. Temporal and spatial variations of microplastics in roadside dust from rural and urban Victoria, Australia: implications for diffuse pollution. *Chemosphere* 252, 126567.
- Wang, G., Lu, J., Li, W., Ning, J., Zhou, L., Tong, Y., Liu, Z., Zhou, H., Xiayihazi, N., 2021. Seasonal variation and risk assessment of microplastics in surface water of the Manas River Basin, China. *Ecotoxicol. Environ. Saf.* 208, 111477.
- Wanger, J., Wang, Z.M., Ghosal, S., Murphy, M., Wall, S., Cook, A.M., Robberson, W., Allen, H., 2019. Nondestructive extraction and identification of microplastics from freshwater spot fish stomachs. *Environ. Sci. Technol.* 53, 14496–14506.
- Yukioka, S., Tanaka, S., Nabetani, Y., Suzuki, Y., Ushijima, T., Fuji, S., Takada, H., Tran, Q.V., Singh, S., 2020. Occurrence and characteristics of microplastics in surface road dust in kusatsu (Japan), da nang (vietnam), and kathmandu (Nepal). *Environ. Pollut.* 256, 113447.
- Zayen, A., Sayadi, S., Chevalier, C., Boukthir, M., Ismail, S.B., Tedetti, M., 2020. Microplastics in surface water of the Gulf of Gabes, southern Mediterranean Sea: distribution, composition and influence of hydrodynamics. *Estuar. Coast Shelf Sci.* 242, 106832.