Doctoral Dissertation

Microplastic pollution in the marine and riverine environments in Yamaguchi: Abundances and distributions, sources-to-sinks, and ecological risks

山口の沿岸と河川環境中のマイクロプラスチック汚染：量と分布，流出過程，生態リスク

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Thesis in One Sentence

This PhD thesis addressed current knowledge gaps regarding microplastic pollution as well as developed new insights into occurrences and fate of microplastics within marine and freshwater systems, prominent sources-to-sinks phenomena, and ecological risk assessments with global relevance.

Abstract

Microplastics (i.e., the tiny plastic particles < 5000 μm) have been regarded as the pollutants of emerging threats for the planetary health. Scientific attentions surged to the microplastic pollution issues recently in the last decade after understanding the presence of microplastics in all the environmental compartments. Microplastic pollution in the aquatic environments (marine and freshwater) are ubiquitous globally. However, to date, there exists critical knowledge gaps regarding the microplastic pollution, occurrences and fate of microplastics within marine and freshwater systems, pollution sources-to-sinks and ecological risks. This study explored microplastic pollution in the Japanese marine and riverine environments in Yamaguchi Prefecture focusing abundances and distribution, characterization, and the occurrences and fate of microplastics within the marine and riverine systems; investigated the sources-to-sinks phenomena and environmental behavior of microplastics while the rivers are the transportation pathways of land-sourced microplastics to the marine systems; and assessed ecological risks.

At the first part, this study investigated microplastic pollution in the Seto Inland Sea (SIS) and Sea of Japan (SJ) surrounded Yamaguchi prefecture areas in Japan. The density separation method was applied to extract microplastics from sea surface sediment and water samples. Polymeric compounds were identified through attenuated total reflectance-Fourier transform infrared spectroscopy analysis. The average microplastic abundances were 112.57±121.30 items·kg^{-1} in sediment and 57.46±20.82 items·L^{-1} in water. Abundance comparisons revealed similar level of pollution in both sea areas and medium to high-level pollution than others. Characterization revealed that fragments and small microplastics (<1000 μm) predominated sediments. Fragments and films were major shapes in the SIS sediments while only fragments predominated the SJ sediments. Large microplastics (1000–5000 μm) fibers predominated water in all the areas. Transparent microplastics predominated both the sediments and water. Polyethylene, polyvinyl alcohol, and polypropylene were major polymers in sediments while polyethylene terephthalate and polyethylene predominated water. No significant correlations of microplastic abundances and characteristics were observed between sediment and water. Anthropogenic activities and environmental factors were speculated to be the main sources of microplastics in these areas. Based on the field observation, this study suggested that the Japan land-sources as well as the regional territory through transboundary fluxes of (micro-)plastics might affect the pollution occurrence in the SIS and SJ marine environments. Overall, this study indicated that microplastic pollution in these marine areas could be an alarming environmental problem. This was the first report regarding microplastic pollution along the SIS and SJ coasts in the Yamaguchi Prefecture, Japan.

At the second part, this study explored microplastic pollution in the riverine water environment. Rivers are vital for understanding freshwater microplastic pollution, along with the conduits from land-sources to marine-sinks. Specifically, this was the first study to investigate microplastic pollution in the small-scale rivers. The small-scale rivers— Awano and Ayaragi, which flow into the Sea of Japan (SJ), and the Asa and Majime rivers, which flow into the Seto Inland Sea (SIS) in Yamaguchi Prefecture, Japan. Surface water samples were collected from 29 stations. Filtration, wet peroxidation, and density separation methods were employed to extract microplastics. Polymers were identified via attenuated total reflectance-Fourier transform infrared spectroscopy. Microplastic abundances and comparisons among them revealed that the small-scale Japanese rivers were more polluted than others around the world. Characterization demonstrated that small microplastics (<1,000 μm) in size, fibers and fragments in shape and the polymers— polyethylene, polypropylene, vinylon, polyethylene terephthalate, and polystyrene were

dominant. Both point and non-point sources could release microplastics into the riverine environments. The small-scale rivers emitted substantially higher quantities of microplastics (0.4–154.27 billions/day and 0.01–17.55 tons/day) into the SJ and SIS environments than larger rivers in other regions. The pollution load index indicated that all the river stations were polluted with microplastics. An assessment of the polymeric and pollution risks revealed variably low to high risks. The higher were the abundances of microplastics and toxic polymers, the higher were the pollution level and risks. The sites at high risk of pollution were regarded as hotspots. Risk-zones and hotspots identification indicated that both point, and non-point sources might affect posing high risks. Moreover, the pollution characteristics indicated that pollutants posed serious ecotoxicological threats to the rivers and their downstream environments. This study provides new insights into riverine microplastic pollution and revealed small-scale rivers to be prominent conduits of sources-to-sinks. Our risk assessments also provided a baseline for future comprehensive assessments and practical approaches to pollution management.

The final part of this thesis describes about microplastics in the riverine sediment environments. Knowledge of microplastic pollution in small-scale river sediments remained insignificant. This study explored microplastics in the sediments of four small-scale Japanese rivers following—the Awano, Ayaragi, Asa and Majime in the Yamaguchi Prefecture, Japan. Sediment samples were collected from the selected stations (n=23). Density separation, wet peroxidation and total reflectance-Fourier transform infrared spectroscopy methods were applied to analyze microplastics. Large microplastics (1000–5000 μm), fragments in shape, and high-density particles of diverse polymers were dominant. Polyvinyl chloride, polyethylene, and polypropylene were the dominant polymers. Microplastic abundance indicated relatively medium-level pollution compared to larger rivers around the world. The sediment microplastics differed from the ones detected in surface water. Thus, the riverine sediment compartment acted as the sink of microplastics. Scanning electron microscopic (SEM) analysis suggested the presence of weathered microplastics in sediments. In addition, energy dispersive X-ray spectroscopic analysis (EDX) revealed metal contaminants on the microplastic surfaces, indicating synergistic hazard potentials in the riverine ecosystems. An assessment of the ecological risks suggested variably low to very high risks of microplastic pollution for the rivers. The elevated ecological risks were due to the higher abundances of microplastics and highly toxic polymers. Polyvinyl chloride, acrylonitrile butadiene styrene, polyurethane, and polymethylmethacrylate were the detected highly toxic polymers. Urban and highly populated land-use sources might influence the generation of 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 of the pollution for riverine environments, as well as is a baseline for further comprehensive risk assessment and developing practical approaches for pollution control and management.

Overall, this study developed new insights into the occurrences and fate of microplastics within marine and freshwater systems, sources-to-sinks phenomena, and ecological risk assessment with global relevance, and was first to fill up the knowledge gaps regarding small-scale river microplastic pollution, their ecological risks.

Keywords: abundance, characterization, conduits, ecological risk assessment, marine microplastic pollution, non-point source, point source, pollution load index, Sea of Japan, Seto Inland Sea, small-scale riverine microplastic pollution, sources-to-sink, sediment, water,

学 位 論 文 要 旨

マイクロプラスチック汚染への懸念が増大している．日本は世界的な経済大国の一つであり、マイクロプラスチック汚染は最重要課題として認識されている．日本の瀬戸内海（SIS）と日本海（SJ）は、マイクロプラスチック汚染のホットスポットと見なされており、山口県はその両方に接している． 2018 年、環境省は山口が日本全国で最も海洋ゴミが多い県であると認定したが、マイクロプラスチック汚染の状況についてはこれまで報告されていない．本研究では、山口県の SIS および SJ 沿岸地域おけるマイクロプラスチック汚染を初めて調査した．その結果、海外の海洋環境と比較して高レベルの汚染が見つかった．マイクロプラスチックの種類（形状−サイズ−色−材質）は、環境マトリックス（海水と堆積物）と空間スケール（SIS および SJ 領域）の両方で異なっていた．堆積物中ではより小さなマイクロプラスチックフラグメント（<1000μm）が優占し、水中では様々な材質のより大きなマイクロプラスチック繊維（1000-5000μm）が優占した．堆積物の方が水より汚染されており、その原因として、より複雑な物理生物的要因が推測される．また、日本国内のマイクロプラスチック発生源が SIS に影響を及ぼし、海外から漂着する（マイクロ）プラスチックが SJ に影響を与えている可能性が示され、全体として、マイクロプラスチック堆積物の評価結果は海洋ポリマーの脅威を示した．この調査を通じて、マイクロプラスチック汚染発生源からシンクに至る経路の研究の必要性が示された．

続いて、山口県内の河川において陸域で発生したマイクロプラスチックが海に至る過程での濃度変化を調査した．山口県内の小規模な河川では、海外のより大きな河川と比較して、マイクロプラスチックで高度に汚染されていることを見出した．小規模な河川のマイクロプラスチック汚染の報告は少なく、文献のギャップを埋める最初の研究であると思われる．マイクロプラスチックの特性評価により、多様なポリマーからなる 1000μm 未満の繊維とフラグメントが河川水で優占していることが明らかになった．また日本で開発された「ビニロン」のマイクロプラスチックが世界で初めて検出された．この調査を通じて、小規模な河川が、日本国内の陸域から供給される多量のマイクロプラスチックを海域に輸送する経路となっていることが明らかになった．今回の調査河川は流域面積は小さいものの、マイクロプラスチックの生成と海洋汚染への影響においては重要であった．ただし、河川に排出されたマイクロプラスチックはそのまま海に至るわけではなく、一部は河川堆積物に移行し、複雑な濃度変化を示しながら海に至ることが明らかになった．河川水と堆積物の間のマイクロプラスチックのやりとりはこれまでほとんど報告されておらず、知識のギャップを埋める成果である．特に堆積物中には大きな粒子（>1000μm）の破片およびフィルムや高密度ポリマーが多く含まれており、河川水とは異なる組成を示した．さらに、河川環境中のマイクロプラスチックは、風化過程を経ることで、粒子表面に金属汚染物質を吸着し、化学物質だけではない相乗的な危険をもたらす可能性があることが観察された．以上のように、本研究は初歩的な段階

ではあるが、河川と海洋のマイクロプラスチックの運命や輸送に関する知識のギャップを埋めることに寄与した.

次に、淡水・海洋生態系への生態毒性リスク評価手法を検討した．マイクロプラスチックの存在量に関する研究は多いが、生態学的リスクの解明は進んでいない．この問題に対応するため、マイクロプラスチックの材質毎の毒性の相違を考慮したリスク評価式を開発した．この式を使用することで、マイクロプラスチック存在量と生態学的リスクはかならずしも連動しておらず、有毒ポリマー量の多寡が問題であることを導出した．この評価式により、山口県の河川と沿岸におけるマイクロプラスチック汚染の生態学的リスクには大きな幅があることが示され、河川の下流域は、上流に比べて生態学的リスクが高い傾向があった．マイクロプラスチックへの人間の曝露は、飲料水供給、食料品、水産業、農業などのさまざまな経路を通じて生じ得ることが推測された.

全体として、本研究により、1. 海洋および淡水システム内でのマイクロプラスチック汚染についての知識のギャップを埋めることに貢献した． 2. 小規模河川におけるマイクロプラスチックの挙動に関する知識のギャップを埋めた．３．日本に特有のポリマーを特定した．４． 山口県のマイクロプラスチック挙動について主要なソースからシンクへの経路を明らかにした． 5.生態学的リスク評価式を開発した．この論文は、「グローバルに考え、ローカルに行動する」という一般的な哲学に照らして、日本のみならず世界のマイクロプラスチックの汚染制御と管理戦略の開発に貢献するだろう.

Statement of Originality

The results submitted in this research are entirely of the candidate's own investigation and no part of the result has been accepted for any other degree, nor is being currently submitted for any other degree. To the best of my knowledge and belief, the thesis contains no results previously published or written by another person except where due reference is made in the thesis itself.

(Signed) ____A. H. M. Enamul Kabir_____

(Date) 15 February 2022

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A. H. M. Enamul Kabir, Masahiko Sekine, Tsuyoshi Imai, Koichi Yamamoto, Ariyo Kanno, Takaya Higuchi. Assessing Small-Scale Freshwater Microplastics Pollution, Land-use, Source-to-Sink Conduits, and Pollution Risks: Perspectives from Japanese Rivers Polluted with Microplastics. Science of The Total Environment, 2021, 144655. https://doi.org/10.1016/j.scitotenv.2020.144655 (Chapter 3)

A. H. M. Enamul Kabir, Masahiko Sekine, Tsuyoshi Imai, Koichi Yamamoto, Ariyo Kanno, Takaya Higuchi. Microplastics in the Sediments of Small-scale Japanese Rivers: Abundance and Distribution, Characterization, Sources-to-sink, and Ecological Risks. Science of The Total Environment, 2022, 152590. https://doi.org/10.1016/j.scitotenv.2021.152590 (Chapter 4)

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A. H. M. Enamul Kabir, Masahiko Sekine, Tsuyoshi Imai, Koichi Yamamoto. Marine Microplastics Pollution in the Yamaguchi Prefecture of Japan: Identification, Characterization and Abundance Comparison. Water and Environment Technology (WET) Conference, Osaka University, 13—14th July 2019, Osaka, Japan.

Chapter 1: Introduction

This chapter introduced the rationale and background of (micro-)plastic pollution and concerns, microplastic sources and occurrences, as well as the sources-to-sinks and pathways along with describing the identified knowledge gaps regarding the pollution in the context of marine and riverine rnvironments, and ecological risks based on the existing published literature. Besides, this chapter includes the overall objectives of this thesis which were considered based on the background of the microplastic pollution and identified knowledge gaps. Besides, this chapter includes the thesis contents and structure. Overall, the Chapter 1 provided a rationale and overview of this study.

1.1. Background

1.1.1. Plastic Pollution

Plastics, which are composed of synthetic polymers, has entered in all aspects of our modern daily life. The application and use of plastics are ubiquitous, with numerous benefits and advantages (low-cost, durable, and resistant, waterproof, light weight etc.) to daily life, society, and the economy (Andrady and Neal, 2009; Plastics Europe, 2019). There has been a continually increasing trend in plastic production and consumption since the mid-20th century. In 2018, 359 million tons of plastics were produced globally, with Asia accounting for 51% of all plastics worldwide (China: 30%; Japan: 4%; other Asian nations: 17%) (Plastics Europe, 2019). However, the impacts of plastics on the environment have also become increasingly apparent. The greatest concerns are the plastics wastes accumulation on the earth and occurrences of global plastics pollution. Aquatic environments are polluted with plastics worldwide (GESAMP, 2016; van Emmerik and Schwarz, 2020). About 4.8—12.7 million tons of plastic were dumped into the oceans in 2010, with this number projected to rise by an order of magnitude by 2025 (Jambeck et al., 2015) and will get tripled by 2040 without taking proper actions immediately (Lau et al., 2020). The marine plastic pollution exhibits the ecological, biogeochemical, and physical thresholds. Thus, plastic pollution is regarded as growing planetary boundary threat (Villarrubia-Gómez et al., 2018).

1.1.2. Microplastic Pollution and Concerns

The tiny plastic particles (< 5000 μm) are termed as microplastics (MPs)— a class of plastic pollutants (Arthur et al., 2009; Thompson et al., 2009; Frias & Nash, 2019). Today, MPs are found present in all environmental components— air, water, biota, soil, and sediments (Büks & Kaupenjohann et al., 2020; Gasperi et al., 2018; Van Cauwenberghe et al., 2015; de Sá et al., 2018; O'Connor et al., 2019; Li et al., 2018; Auta et al., 2017). Scientific attentions surged recently in the last decade to the MP pollution issues after the ubiquitous presence of MPs in the aquatic (freshwater and marine) and terrestrial systems has been reported globally (Fig. 1.1). The abundances, distributions, types, and characteristics (i.e., shape, size, color, and polymer type) of marine MPs pollution, and the potential ecotoxicological threats posed by MPs have been the focus of research and are globally well-reported (Andrady, 2011; Cole et al., 2011; Auta et al., 2017; Peng et al., 2020). Overall, MP pollution has been a concern of severe environmental degradation, ecotoxicological threats and impacts across the marine environments (Andrady, 2011; Auta et al., 2017; Cole et al., 2011; Peng et al., 2020; Wright et al., 2013).

MP pollutants are diverse in characteristics (shapes-sizes-colors-polymers) as well as toxic, pervasive and threatening to biotic and abiotic components of the earth (Rochman et al., 2019; Lambert and Wagner, 2018; Gallo et al., 2018). MPs comprise a long-lived and diverse suite of pollutants that vary in shape, size, color, polymer type, plasticizer, stabilizer, colorant, and other attributes. MPs are also able to adsorb other eco-toxins, including persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals, DDTs, PFAS, pharmaceutically active antibiotic compounds (Wang et al., 2020; Llorca et al., 2018; Li et al., 2018), inorganic metal contaminants (Yu et al., 2019), and microbial pathogens—antibiotic resistant bacteria and genes (Zhang et al., 2020; Liu et al., 2021) and easily spread via long-range transport in aquatic environments. Thus, MPs may be transferred through food webs and their exposure to all biotic and abiotic

matrices is unavoidable (Rochman et al., 2019; Yu et al., 2019; Gallo et al., 2018; Oliveira et al., 2019; Carbery et al., 2018; Hale et al., 2020). There are highly toxic MP polymers which might pose long-lasting toxicity to aquatic life as well as they might cause carcinogenic and mutagenic hazards to human health (Lithner et al., 2011). Lithner et al. (2011) classified plastic polymers as carcinogenic and mutagenic to humans, as well as highly toxic to aquatic life, with long-lasting effects. MPs leach plastic containing toxic chemicals i.e., monomers, additives, and plasticizers (Chen et al., 2019; Gallo et al., 2018; Zimmermann et al., 2020). Consequently, the MP pollutants pose synergistic hazards and enhanced toxicity to aquatic ecosystems.

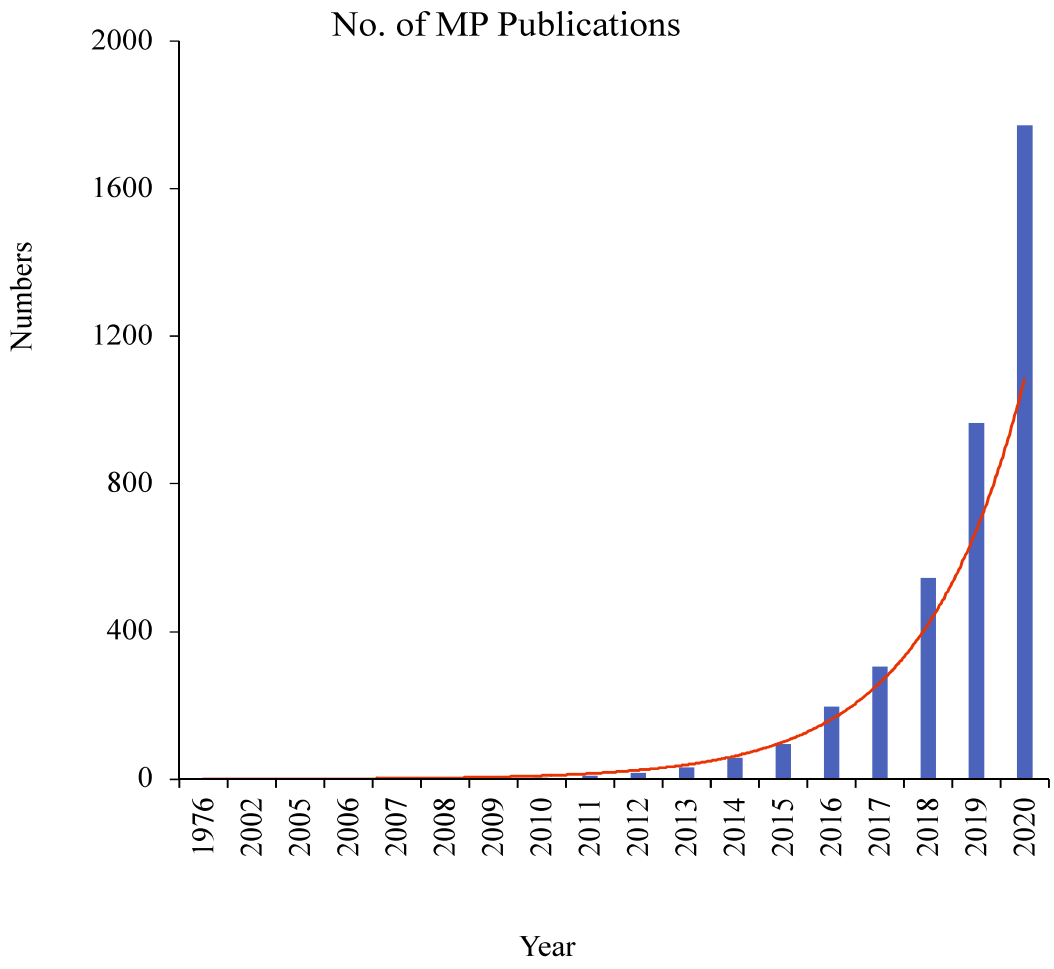

Fig. 1.1 Numbers of microplastics pollution publications as the scientific literature (Source: PubMed; Access: 27th May 2021)

The aquatic (both marine and freshwater) sediments, water and biota are evident as the sink of MPs. MPs exist in many different characters– shapes, sizes, colors and polymers (Auta et al., 2017). MPs poses detrimental hazards and toxicity to marine organisms by uptake, ingestion and contact as well as have been speculated for marine environmental quality deterioration. Thus, MPs may cause chemical toxicity and toxins bioaccumulation in the marine environment (Wright et al., 2013; Rochman et al., 2013; Tanaka et al., 2016; Lusher et al, 2013; Li et al., 2018). Besides, trophic transfer of MPs in the food web may result

in enhanced ecological toxicity. In addition, human health concerns are also suspected through the accumulation of MPs and associated toxins in the food chain through the environment. Further to that, the hazardous MPs polymeric compounds are long-persisting and easily spreading for long-range transport in the environment (Gallo et al., 2018; Oliveira et al., 2019; Carbery et al., 2018). Consequently, the MPs are posing environmental and human health threats. Thus, the emerging marine MPs pollution is an alarming threat towards global environmental protection and sustainability.

1.1.3. Sources, Occurrences, Sources-to-sinks, and Pathways

MPs are sourced on land from the manufacturing of plastic particles, including personal care products, agricultural fertilizers, household and industrial detergents, cleaning products, and paints (primary MPs), and from the fragmentation of larger plastics (secondary MPs) under different environmental conditions (e.g., exposure to sunlight and oxidants, mechanical abrasion, weathering, degradation, etc.) (Cole et al., 2011; Andrady, 2011; Jambeck et al., 2015; Gewert et al., 2015; Scudo et al., 2017). Riverine and marine systems receive MPs from land-based point and non-point sources (Jambeck et al., 2015; Siegfried et al., 2017; Kataoka et al., 2019; Baldwin et al., 2016). Several studies have indicated that the land-use characteristics of point sources (i.e., population density, urban and residential areas, domestic sewage, wastewater treatment plants (WWTPs), industries, etc.) affect the occurrence of MPs pollution (Kataoka et al., 2019; Murphy et al., 2016; Lechner and Ramler, 2015), while other studies have indicated that they have no significant impact (Nel et al., 2017; Klein et al., 2015; Vaughan et al., 2017). Land use related to non-point pollution sources (e.g., agricultural, atmospheric transportation, fallouts and deposition etc.) might also be major contributors of aquatic MPs (Dris et al., 2016; Baldwin et al., 2016; Allen et al., 2019; Huang et al., 2020; Ouyang et al., 2020; Qiu et al., 2020; Dris et al., 2018).

Marine environments are thought to be the largest sink of land-sourced MPs (Jambeck et al., 2015), while rivers are plastic pollution hotspots and serve as the major conduits of land-sourced MPs emissions into the marine realm (Horton and Dixon, 2018; Jambeck et al., 2015; Lebreton et al., 2017; Schmidt et al., 2017; Bowmer and Kershaw, 2010). It has been estimated that ~80% of plastics in the sea are sourced from the land and emitted by rivers (Jambeck et al., 2015; Bowmer and Kershaw, 2010). In modeling studies, Lebreton et al. (2017) estimated 1.15 and 2.41 million tons of MPs enter the ocean via rivers, while Schmidt et al. (2017) predicted the export of between 5×10^{-4} and 6.3×10^{3} tons of MPs per day by the largest river catchments of the world. Lechner et al. (2014) estimated the micro- and meso-plastic litter inputs to be 4.2 tons per day from the Danube River into the Black Sea. On the one hand rivers are initial sink of land-sourced MPs, on the other they are the major conduits to emit land-sourced MPs into the ultimate sink i.e., marine realm (Horton et al., 2017; Jambeck et al., 2015; Lebreton et al., 2017; Schmidt et al., 2017; Simon-Sánchez et al., 2019). However, to date, less are known about river MP pollution (Dris et al., 2015; Blettler et al., 2018; Horton et al., 2017). The sediments, water and biota are the prominently major components for the MPs in the river environments (Li et al., 2018; Yang et al. 2021; O'Connor et al., 2019). While flowing waters constantly discharging river MPs to sea, the riverbed sediments are prone to retain MPs. In fact, there are increasing abundances of MPs in river sediments, said as the MPs accumulation hotspots (Mani et al., 2019; Klein et al., 2015; Nizzetto et al., 2016; Simon-Sánchez et al., 2019).

Table 1.1 Plastic polymers, their monomers, density, uses and applications

Polymers	Abbreviations	Monomer	Density	Applications
Polyethylene	PE	Ethylene	0.91 – 0.96	Reusable bags, trays and containers, agricultural firm, food packaging film, toys, milk bottles, shampoo bottles, pipes, houseware (Plastics Europe, 2019)
Polypropylene	PP	Propylene	0.85 – 0.94	Food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, bank notes, etc. (Plastics Europe, 2019)
Nylon 6		ε-caprolactam	1.14 – 1.15	Textiles, packaging, engineering, medical, and agriculture for having UV absorption capacity (Hu and Yang, 2000)
Vinylon		Vinyl acetate	1.19	Japanese Traditional Dresses, Working Wear, Fishing Nets, seaweed farming nets, Ropes, Filter Cloth, Canvas, Sheets, Cement Reinforcement Material, Hoses, Belts, Tire Cords, Kanreisha (Open Thin Fabric), Threads for Tatami Mats, Construction Nets, Paper Making Felts, etc. (JCFA)
Polyethylene Terephthalate	PET	Ethylene Glycol	1.38	Bottles for water, soft drinks, juices, cleaners (Plastic Europe, 2019)
Polystyrene	PS	Styrene	0.96 – 1.05	Food packaging (dairy, fishery), building insulation, electrical & electronic equipment, inner liner for fridges, eyeglasses frames, etc (Plastic Europe, 2019)
Polyphenylene Sulfide	PPS	1,4-dichlorobenzene	1.35	Synthetic fiber and textiles, coal boilers, papermaking felts, electrical insulation, film capacitors, specialty membranes, gaskets, and packings (Yan, 2016)
Epoxy Resin	EP	Glycidyl-based epoxy resins	0.9–1.1	Manufacture of adhesives, plastics, paints, coatings, primers and sealers, flooring and other products and materials for building and construction, electronic materials (Verschoor et al., 2016; Jin et al., 2015)
Ethylene propylene diene monomer	EPDM	Ethylene, propylene, and diene comonomer	1.5	Synthetic rubber roofing membrane automotive and construction industries, electrical, tire (Holden, 2017)
Polyacrylonitrile	PAN	Acrylonitrile	1.184	Hot gas filtration systems, outdoor awnings, sails for yachts, and fiber reinforced concrete. Fiber copolymers to make knitted clothing, like socks and sweaters, tents textiles, ultra-filtration membranes, hollow fibers for reverse osmosis, etc. Wrapping materials for foods such as tea, coffee, rice, fish, and eggs, and chemicals, drugs, electronics, and cosmetics (Sada et al., 2014).

Table 1.1 Plastic polymers, their monomers, density, uses and applications (Continued)

Polymers	Abbreviations	Monomer	Density	Applications
Polybutylene terephthalate	PBT	Dimethyl terephthalate	1.30	Packaging, automotive, electrical, and consumer markets, optical fibers (Plastics Europe, 2019).
Polycaprolactone	PCL	ε-caprolactone	1.145	Scaffolds in tissue engineering, microparticles for drug delivery, making trash bags, microelectronics, adhesives, and packaging (Labet and Thielemans, 2009).
Polyvinyl Alcohol	PVA	vinyl acetate	1.19	Industries, such as textile, paper industry, and food packaging industry (Satoh, 2014).
Acrylonitrile Butadiene Styrene	ABS	Styrene	1.02 – 1.08	Automotive applications, pipes, toys, electrical, households, 3D printing etc. (Begum et al., 2020; McKeen, 2018)
Polyvinyl chloride	PVC	Vinyl chloride	1.16 – 1.58	Building and constructions, electrical/electronic uses pipes, floor coverings, cable insulation, roofing sheets, packaging foils, bottles, medical products, water supply distribution systems, medical applications, food packaging, industrial hoses, gaskets, elastic automotive parts, electrical cable covers etc.
Fluorinated ethylene propylene	FEP	Ethylene propylene	2.1–2.3	Cables for chemical platoon heating tapes foils filaments and cables at coating for valves, tubes, vessels and tanks electrical applications as terminal blocks and valve and tube holders. non-stick applications in food processing
Polyurethane	PUR	Propylene oxide	1.2	Polyurethane apparel- manmade skin and leathers, garments, sports clothes, sports shoes common sports equipment (soccer balls, judo mats, and binders on running tracks sports flooring) major appliances, rigid foams for refrigerator and freezer thermal insulation systems, car seats, bumpers, car bodies, spoilers, doors, and windows, household floors, flexible foam padding cushions, buildings and constructions, surface coatings, adhesives, solid plastics, and athletic apparel, resilience foam seating, wheels and tires (such as escalator, shopping cart, elevator, roller coaster and skateboard wheels).
Polybutene	PB	1-butene, 2-butene, and isobutylene	0.95	Personal care products, cosmetics, automotive sealants, adhesives, extenders for putties used for sealing roofs and windows, coatings, polymer modification, agricultural films, coatings etc.

1.1.4. Knowledge Gaps: Microplastic Pollution in the Marine and Riverine Environments, and Ecological Risks

Japan, one of the mega economies of the world, has a long history of invention, industrial development, uses and applications of plastics. Today, MP pollution is regarded as the influential problem of paramount importance for the country (Isobe et al., 2015). In the recent years, abundances and distributions of MPs have been reported from the Asian, Pacific, Atlantic, and Arctic seas (Mu et al., 2018), and the East Asian seas have been said as the hot spots of MPs. However, less MPs pollution information have been established in the contexts of the East Asian 'Sea of Japan (SJ)' and 'Seto Inland Sea (SIS)' marine areas in Japan while the seas are regarded as MPs pollution hotspots (Isobe et al., 2015). Moreover, these marine areas are of larger geographical and environmental context in global perspectives (Isobe et al., 2015). Out of the 47 prefectures of the country, Yamaguchi prefecture is surrounded by both the SIS and SJ, which is the most western part of 'Honshu Island, Japan' and was my study area. In the year of 2018, Ministry of the Environment of Japan reported largest amount of marine litter in the Yamaguchi prefectural coasts among all other prefectures. On the other hand, the SJ side of the prefecture is transitional to other country's (South Korea and China) marine areas. However, no MPs pollution information were known so far in the Yamaguchi prefectural marine environmental contexts.

Until now, freshwater MP pollution knowledge are limited globally (Blettler et al., 2018; Li et al., 2018; Kataoka et al., 2019). Scientific investigations started expanding recently towards MP pollution in freshwater environments. In recent studies, MP abundances were observed in biota, sediments and water of freshwater streams, rivers, reservoirs, lakes, wetlands, ponds etc. (Fischer et al., 2016; Kumar et al., 2021; Eriksen et al., 2013; Horton et al., 2017; Rodrigues et al., 2018; Liu et al., 2019; Bordós et al., 2019; O'Connor et al., 2019). Thus, the freshwater ecosystems are also facing huge threats of the (micro-)plastic pollution (Szymańska & Obolewski et al., 2020). So far, little is known about Japanese river MP pollution. Furthermore, rivers are MP pollution hotspots globally and facing numerous ecological threats (Eerkes-Medrano et al., 2015; van Emmerik and Schwarz, 2019; Schmidt et al., 2017; Krause et al., 2020; Simon-Sánchez et al., 2019). Rivers provide the highly dynamic environments for the MP pollutants (Cheung et al., 2018). River-to-marine MP emissions are critical for understanding the transformation, fate, and loadings of plastic pollution from land sources to marine sinks. To date, studies on the MPs emissions from rivers to oceans have been limited (Horton et al., 2017; Hurley et al., 2018). Besides, rivers are not the sole pathways of exporting land-sourced (micro-)plastics, rather river 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. Further to that, MPs pollution in small-scale freshwater bodies is more serious than in coastal waters (Hu et al., 2018; Luo et al., 2019). Yet the MP pollution in small-scale rivers and their quantitative MP emissions remain almost unknown. Particularly, MPs pollution in Japanese rivers remains insignificant largely.

MPs are posing risks to the environment and human health (Rochman et al., 2015; Burns and Boxall, 2018; Galloway, 2015; Koelmans et al., 2017; Koelmans et al., 2017; Wright and Kelly, 2017; Eerkes-Medrano et al., 2015). Despite the wide abundance of MPs in aquatic environments, existing knowledge on pollution risks remains limited (Koelmans et al., 2017). What are ecological risks of the MPs to ecosystems,

remains far from understood (Koelmans et al., 2017). Furthermore, the ecological risks knowledge is significant to obtain insight into MPs pollution, threats and impacts in a particular ecosystem as well as apply the knowledge for policy making approaches in pollution control and management. On the other hand, MP pollution risk knowledge are 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, the social responses and problems of risk reduction and management (Kramm & Völker, 2018).

Overall, understanding the marine and riverine MP pollution comprehensively, pollution sources-to-sinks, environmental behavior of MPs, and ecological risks are highly crucial to fill the knowledge gaps in the field as well as develop practical measures for risks reduction, control, and management.

1.2. Thesis Objectives

Overall, the main objectives of this study were—

a) to investigate the marine MP pollution along the SJ and SIS coasts in the Yamaguchi Prefecture areas, Japan.

b) to investigate small-scale riverine MP pollution and identify the potential Japan land-use sources affecting the occurrence of MPs; estimate the MP loadings of the rivers into the SJ and SIS; develop MP pollution insights through measured pollution load indices; assess ecological risks of MP pollution assessments and identify pollution hotspots.

c) to investigate MPs in the sediments of the small-scale Japanese rivers, identify the potential land-use sources affecting MPs occurrences in river sediments, terrestrial sources-to-sinks, assess the ecological risks and identify the hotspots.

1.3. Content and Structure of the Thesis

This thesis begins with a general introduction (Chapter 1) followed by two published journal papers and one to be submitted (Chapter 2,3, 4), a general discussion (Chapter 5), and summarizing the key findings and recommendations (Chapter 6).

Chapter 1: Background, knowledge gaps, objectives, and an overview of the content of this thesis.

Chapter 2: The current state of marine microplastic pollution along the coasts of the Yamaguchi prefecture, through abundances and distribution, characterization, sources and occurrences.

Chapter 3: Assessment of MP pollution in the surface water of the small-scale Japanese rivers; estimating the river-to-marine emission as the sources-to-sink conduit to understand the influences of rivers to cause marine pollution by emitting Japan land-sourced MPs; identify the land-uses to address the preliminary knowledge gaps regarding the freshwater MP pollution occurrence; and assessing the ecological risks of MP pollution.

Chapters 4: MPs in the sediments of small-scale Japanese rivers, sediments as the initial sink of land-sourced MPs, and ecological risks of MP pollution risks to fulfill the preliminary knowledge gaps regarding the freshwater MP pollution as well as understanding the ecological toxicity of riverine MP pollution.

Chapter 5: General discussions.

Chapter 6: Summary and recommendations.

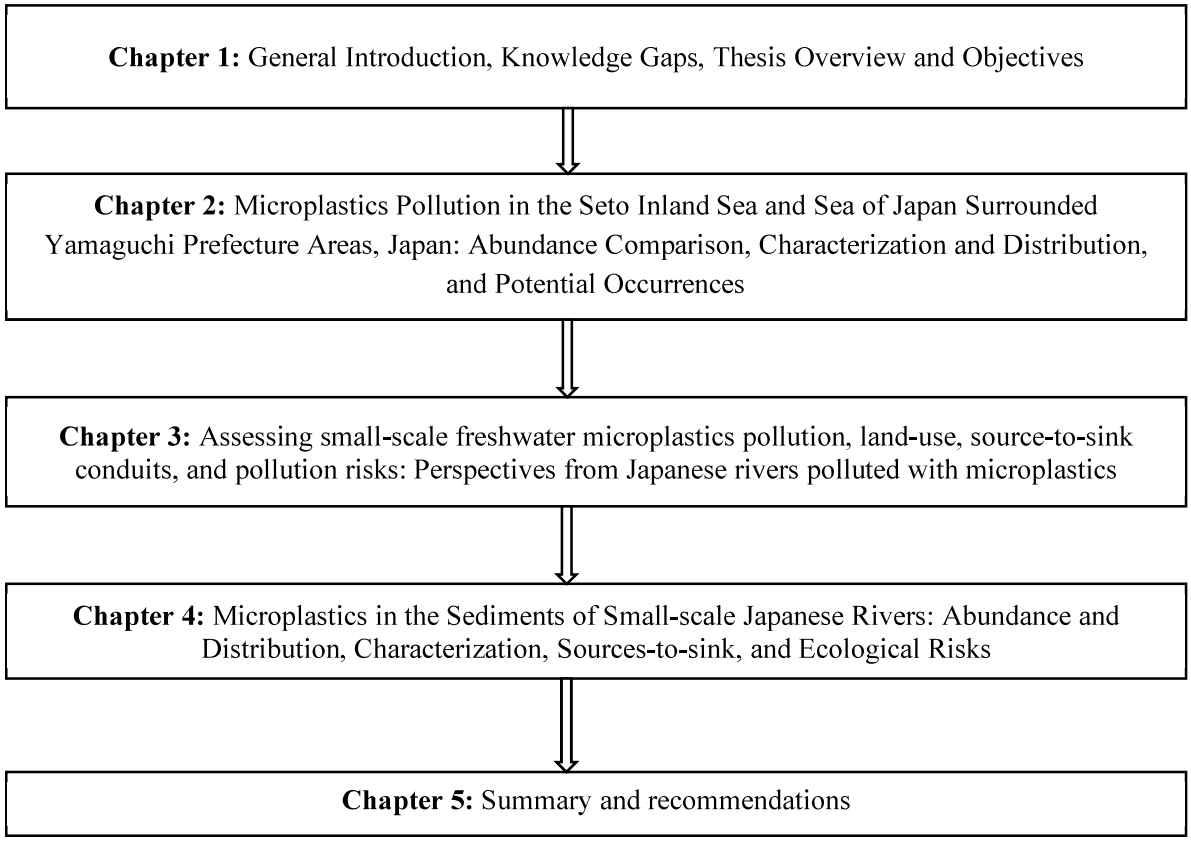

Fig. 1.2 Overview of the content of thesis

[N. B.: Please note that, because each chapter needs to stand alone as a whole manuscript for publishing as a scientific article, there is likely to be some repeat in the introduction among the chapters].

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Chapter 2

Microplastic Pollution in the Seto Inland Sea and Sea of Japan Surrounded Yamaguchi Prefecture Areas, Japan: Abundance Comparison, Characterization and Distribution, and Potential Occurrences

This chapter of the thesis provides a comprehensive literature, identified existing knowledge gaps, current state and concerns of MP pollution knowledge in the context of marine environments along the Yamaguchi Prefecture, Japan. Further to that, this chapter identified knowledge gaps and opened the ways for future studies which are addressed in the following Chapters 3 & 4.

Abstract

Marine microplastic pollution has been an emerging global threat. This study investigated microplastic pollution in the 'Seto Inland Sea (SIS)' and 'Sea of Japan (SJ)' surrounded Yamaguchi prefecture areas in Japan. The density separation method was applied to extract microplastics from sea surface sediment and water samples. Polymeric compounds were identified through attenuated total reflectance-Fourier transform infrared spectroscopy. The average microplastic abundances were 112.57±121.30 items·kg^{-1} in sediment (dry weight) and 57.46±20.82 items·L^{-1} in surface water. Abundance comparisons revealed similar level of pollution among the SIS and SJ sea areas. Medium to high-level pollution was revealed in these marine areas in comparison to other studies around the world. Characterization revealed that fragments and small microplastic particles (<1000 μm) predominated sediments. Fragments and films were major shapes in the SIS sediments while only fragments predominated the SJ sediments. Large microplastic fibers (1000–5000 μm) predominated water in all the areas. Transparent microplastics predominated both the sediments and water. Polyethylene, polyvinyl alcohol, and polypropylene were major polymers in sediments while polyethylene terephthalate and polyethylene predominated water. No significant correlations of microplastic abundances and characteristics were observed between sediment and water. Anthropogenic activities and environmental factors were speculated to be the main sources of microplastics in these areas. Overall, this study suggested that microplastic pollution in these marine areas could be an alarming environmental problem.

Keywords: marine microplastic pollution, abundance, characterization, Seto Inland Sea, Sea of Japan

2.1. Introduction

Plastic, the material of synthetic polymers, has entered in all aspects of our daily life. Plastic materials have a practically unlimited number of advantages and applications (Thompson et al., 2009). There is ever-growing plastic uses and productions (348 million tons in 2018) from the mid-20th century (Plastic Europe, 2018). However, today, the disadvantages of plastics are visible. Marine environments all over the world are polluted with plastics. Microplastics (MPs) i.e. the tiny plastic particles (1–5000 μm) in size, occur from manufactured plastic particles in various products (primary microplastics) and the fragmentation of larger plastic litters (secondary microplastics) under different environmental processes (weathering, UV exposure, biodegradation, and physical stress) (Cole ta al., 2011; Andrady et al., 2011; Auta et al., 2017; GESAMP 2015). Currently, the ubiquitous presence of MPs in the marine aquatic systems has been reported globally, and the marine microplastics (MPs) pollution has been regarded as the threatening form of plastic pollution (Cole ta al., 2011).

The MP abundances, distribution and potential ecological impacts across the marine environments are well reported in recent studies. Mainly, the marine sediments, water and biota are evident as the focus for the MP existence. MP exists in many different characters– shapes, sizes, colors and polymers (Auta et al., 2011; Mu et al., 2018). MP poses detrimental hazards and toxicity to marine organisms by uptake, ingestion and contact as well as have been speculated for marine environmental quality deterioration. Moreover, MP adsorbs persistent organic pollutants (POPs), heavy metals and hydrophobic organic pollutants. Also, MP itself leaches toxic chemical additives. Thus, MPs may cause chemical toxicity and toxins bioaccumulation in the marine environment (Wright et al., 2013; Rochman et al., 2013; Tanaka et al., 2016; Lusher et al., 2013; Li et al., 2016). Besides, trophic transfer of MPs in the food web may result in enhanced ecological toxicity. Human health concerns are also suspected through the accumulation of MPs and associated toxins transfer through the environmental food chain. Further to that, MPs are long-persisting and easily spreading for long-range transport in the environment (Smith et al., 2013; Isobe et al., 2015; Iwasaki et al., 2017; Isobe et al., 2014; Zhang, 2017). Consequently, MPs are posing severe environmental and human health threats. Thus, the emerging marine MP pollution is an alarming threat towards global environmental protection and sustainability.

In the recent years, abundances and distributions of MPs have been reported from the Asian, Pacific, Atlantic, and Arctic seas (Mu et al., 2018). The East Asian seas have been said as the hot spots of MPs. However, less MP pollution information have been established in the contexts of the East Asian 'Sea of Japan (SJ)' and 'Seto Inland Sea (SIS)' marine areas in Japan. Isobe et al. 2014 investigated MP and their transportation processes in the SIS. The mean abundances of oncentration of pelagic MPs around Japan was found 3.7 pieces m^{-3}, which is about 10 times greater in the Seto Inland Sea (0.4 pieces m^{-3}), thus identified as the hotspots of MPs pollution. Moreover, these marine areas are of larger geographical and environmental context in global perspectives (Isobe et al., 2015; Ministry of the Environment, 2018; Hidetaka, 2002). The 'Yamaguchi Prefecture' is the most western part of 'Honshu Island, Japan' which is surrounded by both the SIS and SJ and was the study area. Also, the SJ side of the prefecture is transitional to other country's (South Korea and China) marine areas. There is no MPs pollution information is known along the SJ and SIS coasts in Yamaguchi Prefecture areas. On the other hand, the 'Ministry of Environment (MOE), Japan' conducted marine litter monitoring research in the coastal areas (MOE, 2018). The results indicated that the 'Yamaguchi Prefecture' coasts had the largest amount of marine litter (MOE, 2018).

These emphasized the MP pollution investigation in these prefectural marine environmental contexts. Besides, the SIS has been significantly affected by anthropogenic impacts (Hidetaka, 2002). Importantly, the MPs pollution information are of prior need towards development of pollution mitigation and management strategies, environmental protection, and sustainability. Hence, the main objective of this study was to investigate the MPs pollution through identification, characterization, distribution and abundance comparison along the SJ and SIS coasts in the Yamaguchi Prefecture areas, Japan.

2.2. Materials and Methods

2.2.1. Study Area

The SIS is a semi-enclosed inland sea in Japan (Hidetaka et al., 2002). And the SJ is the large geographical transitional sea between Japan, North and South Korea, China and Russia (Isobe et al., 2015). The Yamaguchi prefecture has the coastlines along both the SIS and SJ. Thus, the study areas were selected along the SIS and SJ coastal areas of Yamaguchi Prefecture, Japan. The Yamaguchi Bay (JY), Shiratsuchi Beach (JS), Chofu Beach (JC) areas were selected from SIS marine areas, and Doigahama Beach (JD) area was selected from SJ side of the prefecture (Fig. 2.1).

2.2.2. Sample Collection

'Standardized protocol for monitoring microplastics in sediments' and 'Standardized protocol for monitoring microplastics in seawater' of 'JPI-Oceans BASEMAN project' guidelines were followed for sampling of sea surface sediments and water (Frias et al., 2018; Gago et al., 2018). In brief, for sampling of sea surface sediments– one kilogram (1 kg) of sea surface sediments (top 5 cm depth) were carefully collected per sampling from each selected area using quadrat ($0.25 \times 0.25 \times 0.05$ m^3) and stainless scoop. Each sample was stored into aluminum foil bag from each sampling site, then transported to laboratory and processed for laboratory analysis.

For sea surface water sampling– there exists both net-based (e.g., plankton nets, neuston nets, bongo nets, manta trawls) and bulk/grab sampling methods. Grab sampling method was employed in this study. Studies reported that the higher mean MP abundances have been found by collecting grab samples than by collecting using net samples in the same survey sea area. This happens mainly because of the commonly used different mesh sizes (>300 μm) of the trawl-nets in which smaller MPs less than the used mesh sizes couldn't be identified and thus, understanding of MP abundances might be hindered by limitations. Moreover, the grab method is suitable for identification of MP fibers from the surface water (Abigail et al., 2017; Green et al., 2018; Gago et al., 2018). We took 1 L of sea surface water from each sampling points.

A total of 46 samples including sediments (n = 28) and water samples (n = 18) were collected for laboratory analysis. The samples from JS area were collected on 18 December 2018 while all other samples form JY, JC and JD areas were collected on 12 February 2019. All sampling materials and apparatus were clean and prepared as well as any possible external contamination was avoided during sample collection.

2.2.3. Sample Preparation and Laboratory Analysis

We followed 'NOAA Laboratory Methods for the Microplastics Analysis in the Marine Environments' along with adjustment to 'Standardized protocol for monitoring microplastics in sediments' and 'Standardized protocol for monitoring microplastics in seawater' of 'JPI-Oceans BASEMAN project' (Frias et al., 2018; Gago et al., 2018; Masura et al., 2015). Overall, the density separation and wet peroxidation (WPO) methods were employed for extraction of MPs from the sea surface sediments and water samples.

Firstly, for the sea surface sediments, the samples were completely dried at 90^0C in oven over 24 hours. Then, the samples were sieved, and any materials greater than 5000 µm were discarded. 500 g of sediments were taken into prepared beaker for density separation. After that 500 mL of prepared Zinc Chloride ($ZnCl_2$) solution of obtained density 1.5 g/cm^3 was poured into the beaker, stirred and allowed at least 24 hours for settling of each sample (Coppock et al., 2017). Then, the supernatant was passed through stainless steel 50 µm sieve and all the floating particles were extracted. The procedure was repeated at least three times. Thus, all the extracted particles (50–5000 µm) were transferred into beaker. At the second step, WPO was done to remove any organic matter and debris from the extracted particles. For WPO, 20 mL of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) solution and 20 mL of 30% hydrogen peroxide (H_2O_2) solution were used as catalysts per each sample and digested at 70^0C on hotplate. After the complete digestion, final density separation was done using the prepared 100 mL filtered $ZnCl_2$ solution for extracting the MPs into different sizes and categories. Following categories of sieves— 50–250 µm, –500 µm, –1000 µm, –2000 µm, and –5000 µm were used as per the mesh sizes for extraction of MPs. The $ZnCl_2$ solution was reused each time through filtration (1 µm PTFE membrane), density checking and adjustment (Coppock et al., 2017).

Secondly, for the preparation of sea surface water samples, we kept the samples at room temperature after collection. At the first step of laboratory analysis, 1 L of sample was filtered using 1 µm PTFE membrane using the vacuum filtration system. After that, the WPO method was employed. Finally, through density separation using $ZnCl_2$ solution, the MPs were extracted from water samples as per the size categories following the same way of the sediment samples processing.

All the necessary laboratory steps were taken to control the external contamination during laboratory analysis. Nitrile gloves and cotton lab gowns were used during the whole experiment. All the materials and apparatus were cleaned with ultrapure water and covered by aluminum foil after each step. Procedural blank tests were carried out during experiment in the laboratory. Each experiment was repeated three times and the filters were placed in a clean glass dish for microscopic examination. Any potential external contamination was avoided during the sampling, laboratory processing and analysis.

2.2.4. Identification and Characterization

After extraction, all particles were visually identified, counted, and measured under a light dissecting microscope (BH2, OLYMPUS, Japan) at 40X magnification. Micro-forceps were used for separation and categorization of MPs according to sizes, shapes and colors. Then, they were transferred to the tared glass vials. Particles counting was done for all categories and characteristics individually. All the images were photographed using the 'OLYMPUS E-500' camera. Finally, the polymer types of the particles

as per the shapes, sizes and colors were identified by Attenuated Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) (FT/IR-6300, JASCO Incorporation Ltd., Japan).

2.2.5. Data Analysis

The reporting units of MPs results were followed as 'items·kg^{-1} for sediments and items·L^{-1} for water following the standardized protocols and published reports (Table 2.2 and 2.3) (Frias et al., 2018; Gago et al., 2018). All the abundances and proportions were calculated based on the number of particles. ArcGIS 10.4.1 was used for MPs distribution analysis in the study sites. All the statistical data analysis was done using Microsoft Excel 2016 and IBM SPSS 22.0. The analysis of correlation of sediment and water MPs data were calculated with 2-tailed Pearson Correlation (significant at *p <0.05). The difference between the abundances and characteristics of the different studied regions were analyzed with the one-way analysis of variance (ANOVA) (significant at *p <0.05).

2.3. Results and Discussion

2.3.1. Abundance and Distribution

All the sampling sites were contaminated with MPs (Fig. 2.1). The MPs abundance ranges varied from 6 to 502 items·kg^{-1} with an average value of 112.57±121.30 items·kg^{-1} in sea surface sediments (n=28). The highest average MP concentrations for sea surface sediment samples was identified in Yamaguchi Bay (JY) followed by the Shiratsuchi Beach (JS) and Chofu Beach (JC) areas of SIS areas. On the other hand, SJ area i.e. Doigahama Beach (JD) was found with a slightly lower MPs concentration than Yamaguchi bay (JY) but higher than other areas of SIS. Although MPs abundance values varied in each site, no greater differences were found between the studied areas. For the sea surface water, the SJ area was found having higher MP abundances than the SIS areas. The SJ area surface water i.e. JD areas had the maximum average MPs concentration. The sea surface water MP abundances were comparatively higher in JS followed by the JC and JY in the SIS areas (Fig. 2.1). All the average abundance values are represented in Table 2.1. Overall, although the SJ side was found having comparatively higher MP abundances than the SIS areas, however no significant (p > 0.05) differences were found to speculate high level MPs pollution in the SJ area than SIS areas. Thus, the overall results indicated the similar MPs pollution level both in the SJ and SIS areas.

On the contrary, significantly higher concentrations of MPs were found per one kilogram (kg) of sea surface sediment than per one liter (L) of sea surface water in this study (p < 0.05) which indicated the higher MP abundances in sediments than water. Similar results of higher MP concentrations in sediments than water was claimed in other studies (Table 2.2 and 2.3). Although environmental processes and factors regarding MPs occurrences and depositions in sea surface sediments and water are not adequately known, it is thought that sediments are the one of the major destinations for MPs and other pollutants in the marine aquatic environments (Bergmann et al., 2017; Woodall et al., 2014). Moreover, the natural conditions (temperature, waves and currents, salinity, or wind, transportations), biofouling and biofilms formations, the density, size and shape of MPs might influence the higher amount of MPs deposition and settlement in sediments than other environmental compartments. Thus, the sediments might be potential to accumulate more MPs (Ling et al., 2017; Zettler et al., 2013; Moret-Ferguson et al., 2010).

Table 2.1 Average MP Abundances in the SJ and SIS Surrounded Areas of Yamaguchi Prefecture, Japan

Study Areas	Sediment (items·kg^{-1}) (Mean ± SD)	Water (items·L^{-1}) (Mean ± SD)
Yamaguchi Bay (JY)	136.33±190.18 (n=6)	32.22±12.67 (n=3)
Shiratsuchi Beach (JS)	102.4±58.08 (n=10)	64.6±18.27 (n=8)
Chofu Beach (JC)	82.2±59.62 (n=5)	57.22±14.98 (n=3)
SIS Areas	108.81±120.24 (n=21)	53.82±20.26 (n=14)
SJ Area, Doigahama Beach (JD)	121.14±132.98 (n=7)	77.50±12.02 (n=4)
Total Average (n=46)	112.57±121.30 (n=28)	57.46±20.82 (n=18)

2.3.2. Abundance Comparison

Numerous studies have investigated the MP pollution in the marine environments. Due to inconsistent MP analytical methods and reporting units, we compared the results with the studies of similar analytical methods and reporting units. The collected MPs pollution information were from both of similar geographical proximate and distant sea areas (Table 2.2 and 2.3). MPs abundances in the sea surface sediment of the SJ and SIS areas were similar with those of similar geographically proximate seas following– the Bohai Sea (China), Hong Kong Sea areas, and coasts of South Korea. Besides, the abundance was one magnitude smaller than Malaysia marine environment and Gulf of Thailand, and one magnitude higher than those Singapore Mangrove Coastline, North Yellow Sea (China), Baltic Sea areas (Germany, Norway, Russia, Poland). However, Tokyo bay sediments, China sea sediment, and North Atlantic sediment had been found to have eighteen to seventy times higher MPs concentration than this study. Overall, these results indicated that both the SIS and SJ surface sediments were medium to highly MPs contaminated than many other marine environments around the world (Table 2.2).

On the other hand, higher abundances of MPs in sea surface water in SJ and SIS areas were found than others around the world. The MP abundances were two magnitude higher than than North Yellow Sea of China, and two to three times lower Jade Bay (Southern North Sea) of Germany. However, sea surface water MPs abundance information is limited in the context of grab water sampling method–based analysis. Further, we also compared sea surface water MPs abundance results with some other freshwater studies of similar methodology. These results show that our results were in same order magnitude of those to Amsterdam Canals (Netherlands), Gallatin river (USA) and slightly higher than Poyang lake, China. Also, our results are eight to ten times higher than Bohai sea, Wei river and Taihu lake of China (Table 2.3). Overall results indicated a higher MPs abundances in sea surface water of these SIS and SJ marine aquatic ecosystems. Although there is no established standard to compare and measure the MP pollution level with ecosystems implications yet, however, overall, medium to high MP abundances in sediment and higher abundances in sea surface water indicated a high-level MP pollution in these areas than others. Such high-level MPs pollution might be the cause of concern regarding marine pollution in Japan.

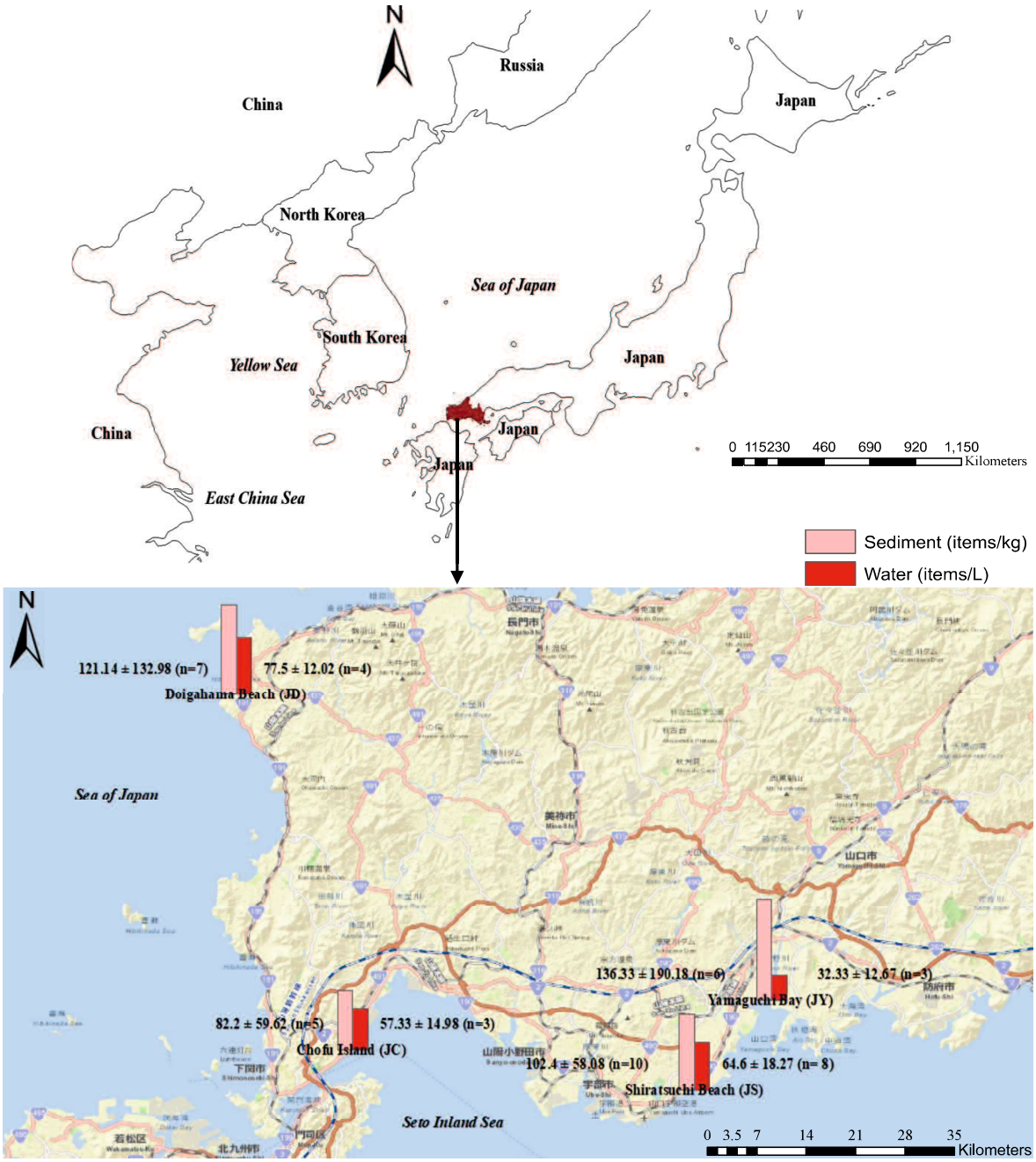

Fig. 2.1 Study Sites and MPs Abundance Distribution in the Study Sites of the Seto Inland Sea (Yamaguchi Bay, Shiratsuchi Beach and Chofu Beach) and Sea of Japan (Doigahama Beach) in the Yamaguchi Prefecture of Japan. Pink and Red Bars Represent the MPs Abundance in the Sea Sediments (items/kg) and Water (items/L) respectively.

Table 2.2 A Summary of MP Abundances in Marine Sediments in Various Seas of the World

Sea	Regions (Sampling Area)	Sediment (items·kg^{-1})	Major Types	Compounds	References
North West Pacific	Japan (Tokyo Bay)	1845[a]	Fragments	PE, PEP	Matsuguma et al., 2017
	South Korea (Korean Coasts)	199.7[a]	Foam	PS, PE, PP	Eo et al., 2018
Asian Seas	SJ	121.14[a]	Fragments	PP, PVA	This study
	SIS	108.81[a]	Fragments, Films	PE, PP	This study
	Singapore	37[a]	Fibers	PE, PP	Nor and Obbard, 2014
	Bohai Sea, China	127[a]	Fibers	PE, PS	Yu et al., 2016
	Malaysia (Straits of Johor)	300[a]	Fragments	PS, PP	Matsuguma et al., 2017
	China	6912[a]	Fibers	PE, PET, PS	Qiu et al., 2015
	North Yellow Sea, china	37.1[a]	Films, Fibers	PE, PP	Zhu et al., 2018
	Hong Kong	47–279[b]	Fragments, Fibers	PE, PP	Tsang et al., 2017)
	Hong Kong	161[a]	Fibers	PE, PP, PET	Lo et al., 2018
	Thailand (Gulf of Thailand)	248[a]	Fragments	PE	Matsuguma et al., 2017
North Atlantic	Germany	88.1[c]	Fibers	—	Hengstmann et al., 2018
	Belgium	390[a]	Fibers	PS, PP	Claessens et al., 2013
	Norway	72[a]	Fibers	PET, PE	Lots et al., 2017
	South Africa	161–759[b]	Fibers	—	(Nel and Froneman et al., 2015
	South Africa (Durban Bay)	1750[a]	Fragments	—	Matsuguma et al., 2017
Baltic Sea	Poland	25–53[b]	Polyester, fibers	—	Graca et al., 2017
	Russia (Kaliningrad)	1.3–36.2[b]	Foam	—	Esiukova et al., 2017
	Tunisia	316[a]	Fibers, Fragments	PE, PP, PS	Abidli et al., 2018
Mediterranean Zone	Spain	100–900[b]	Fragments	—	Alomar et al., 2016
	Italy (Tyrrhenian Sea)	45–1069[b]	Filament	—	Guerranti et al., 2017
	Italy (Tyrrhenian Sea)	62–1069[b]	Black, blue	—	Cannas et al., 2017
	Italy	1512[a]	Fragments	PE, PP	Guerranti et al., 2017
Bering Seas–Chukchi Seas		22.8[a]	Fibers	PP, PET	Mu et al., 2018
Atlantic Ocean		268[a]	Fibers	PET	Woodall et al., 2014

— means 'not reported'. PE: Polyethylene, PVA: Polyvinyl Alcohol, PP: Polypropylene, PET: Polyethylene Terephthalate, and PS: Polystyrene

[a] means the average abundance of microplastics

[b] means the minimum to maximum value of microplastics

[c] means the median value of microplastics

Table 2.3 A summary of MP abundances in surface water in various seas and freshwater systems of the world

Regions (Sampling Area)	Water (items·L^{-1})	Major Types	Compounds	References
SIS, Japan	53.82[a]	Fibers	PET, PE	This study
SJ, Japan	77.5[a]	Fibers	PET	This study
Poyang Lake China	5–34[b]	Fibers	PP, PE	Yuan et al., 2018
Jinhae Bay, South Korea	88[a]	Fragments	PP, PE	Song et al., 2015
Bohai Sea	1.6–6.9[b]	Fibers, Fragments	PP, PE, PS	Dai et al., 2018
North Yellow Sea	0.545[a]	Film, Fibers	PE	Zhu et al., 2018
Jade Bay (Southern North Sea)	152[a]	Fibers, Granules	—	Dubaish et al., 2013
Gallatin River, USA	0–67.5[b]	Fibers	PET	Barrows et al., 2018
Amsterdam Canal, Netherlands	48–187[b]	Fibers	—	Leslie et al., 2017
Wei river, China	3.67–10.7[b]	Film, Fragment	PE, PS	Ding et al., 2019
Pearl River	8.7–53[b]	Film, Fragment	PA, Cellophane	Yan et al., 2019
Taihu Lake, China	3.4–25.8[b]	Fiber	Cellophane	Su et al., 2016

— means 'not reported'. PE: Polyethylene, PA: Polyamide, PP: Polypropylene, PET: Polyethylene Terephthalate, and PS: Polystyrene

[a] means the average abundance of microplastics

[b] means the minimum to maximum value of microplastics

2.3.3. Microplastic Characteristics

2.3.3.1. Shape

The shapes of the observed MP particles were sorted into fragments, films, granules and fibers. The fragments (62.51%) were the predominant shape characteristic in the sea surface sediments followed by films (34.51%), fibers (2.68%), and granules (0.30%) of the totally extracted MPs numbers (Fig. 2.2; Table S2.1). From the environmental distribution point of view, both fragments and films dominated the sediments of the SIS areas. Shiratsuchi Beach (JSS) and Yamaguchi Bay (JYS) areas were found with higher number of films whereas Chofu Beach (JCS) had higher number of fragments in the SIS. On the contrary, almost all the MPs from Doigahama Beach (JDS) of SJ area were fragments (97.88%) surprisingly. The extracted fibers from sediments were mainly from JSS area of SIS. A few granules were found from the studied areas. On the other hand, MPs fibers (70.28%) were the predominant characteristics in sea surface water followed by fragments (18.81%) and films (10.91%) (Fig. 2.2; Table S2.1). Both the SJ and SIS surface water exhibited similar characteristics as per MPs shapes. JYW of SIS had the highest proportion i.e., 87.63% of fibers. Fragments and films were the next dominating characteristics in sea

surface water for all the areas (Fig. 2.2). Moreover, there were no significant correlations significant (*p > 0.05) between the MP shapes in sediment and water (Table S2.3). Further to that, there were noticeable differences in shape-based abundances between the sea surface sediments and water. Fragments and films were dominant in sediments while fibers were dominant in water. As discussed earlier, it could be thought that there are many factors and environmental processes (temperature, waves and currents, salinity, or wind, transportations, biofouling and biofilms formations, the density, size and shape) which might lead to MP deposition, settlement and buoyancy respectively of different MP shapes in the sediments and water. However, the MP deposition and buoyancy mechanism are hindered by lack of adequate information and not yet conclusive (Ling et al., 2017; Zettler et al., 2013; Moret-Ferguson et al., 2010).

Overall, the dominance of the MP fragments, films and has also been noted in sea surface sediments and water in other studies (Table 2.2 and 2.3). The fragments are mainly attributed to the breakdown of larger plastic products (Cole et al., 2011). Films are mainly produced by the fragmentation of plastic carry bags, indicating their disposal, transportation from other areas (Nor and Obbard, 2014). The domestic sewage from washing machine and textile sources might release a vast quantity of fibers in the oceans (Falco et al., 2019). Thus, the identified MP characteristics and their abundances proportions indicated that the studied areas might be affected by these anthropogenic as well as environmental process.

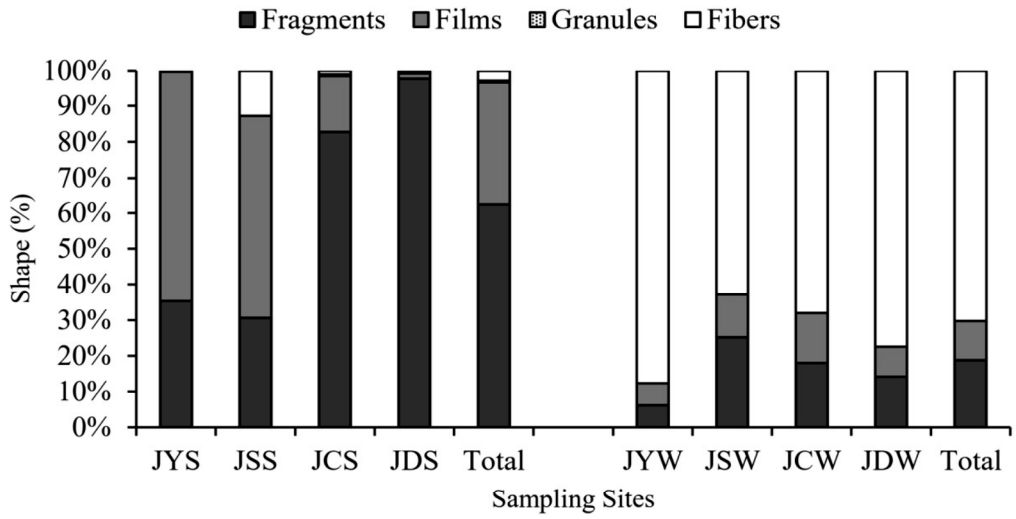

Fig. 2.2 Shape based proportions and distributions of totally extracted MP particles in the sea surface sediments and water in the SIS and SJ areas (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water').

On the other hand, fragments, films and fibers are the common types of MPs found in the marine aquatic organisms while the fibers and fragments are the most common form of MPs as reported in the field studies (de Sa et al., 2018). Studies found the fragments, fibers, and films in the digestive tracts of the marine fishes and their negative impacts were also reported (Tanaka and Takada, 2016; Lusher et al., 2016). MPs ingestion might cause physical damage, intestinal blockage and internal abrasion, and pose numerous ecotoxicological effects (Wright et al., 2013; de Sa et al., 2018). Studies demonstrated that the toxicity of MP fibers is greater than that of other MP particles (Ziajahromi et al., 2017), which may be related to the longer duration of fiber in the intestinal tract (Au et al., 2015; Lei et al., 2018) as well as able to adsorb

other persistent and toxic chemical pollutants (Au et al., 2015; Re, 2019). Moreover, the higher abundances of fragments, films and fibers in the same marine environment poses the higher MPs encounter potential in the inhabiting marine organisms (Fang et al., 2018; Phuong et al., 2018). Thus, the results indicated that the identified different types of MPs shape characteristics (fragments, films, granules and fibers) might pose harmful potentials to cause negative impacts on the marine aquatic systems in the both SIS and SJ areas. However, overall MPs types of shapes-sizes are important for ecotoxicological understandings which are discussed in the following '2.3.3.2 Shape-size' part.

2.3.3.2. Shape-size

Shapes-sizes are important to highlight as a critical factor influencing detrimental effects on the aquatics systems (Eo et al., 2018; Gray et al., 2017). Each of the sediment and water samples were contaminated with different sizes of MPs in this study. Primarily, the size-based results were categorized into small MPs (<1000 μm) and large MPs (1000–5000 μm) (Eo et al., 2018, Frias et al, 2018). The results revealed that the small MPs i.e. <1000 μm occupied the major proportion (76.57%) in the sea surface sediments followed by large MPs i.e. 1000–5000 μm (23.43%) while large MPs i.e. 1000–5000 μm were predominant (60.71%) in the sea surface water followed by small MPs i.e. <1000 μm (39.29%) of totally identified MP particles numbers. Although large MPs predominated the water samples, small MPs abundances were also seen in considerable amount. Overall, the small MPs were the predominant characteristics in this study (Fig. 2.3).

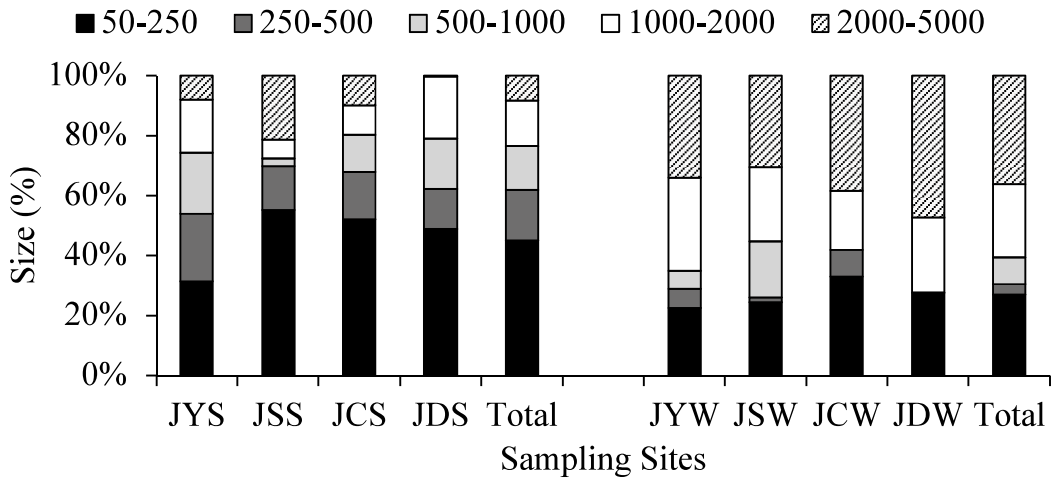

Fig. 2.3 Size based MPs proportions. **a)** proportions in the sea surface sediments, and **b)** proportions in the sea surface water.

Shape-size based characterization results showed that most of the fragments and films were small sized MPs (<1000 μm) while the fibers were large sized MPs (1000–5000 μm) both in the sediment and water (Fig. S2.1). Size-based distribution of MPs indicated that the small MPs dominated the sediments for both the SIS and SJ areas while the large MPs in water. However, comparatively, SJ side sediment was found with higher concentration of small MPs than SIS areas. Also, higher abundances of large MPs abundances were found in SJ water (Fig. 2.4). No significant correlation (*$p > 0.05$) was found between the sea surface sediment and water regarding MPs size-based abundance (Table S2.4).

The dominance of small MPs (<1000 μm) has been found in many other studies (Tanaka and Takada, 2016; Lusher et al., 2016; Eo et al., 2018). The common sizes were found to be small MP fragments in the marine sediments which is consistent with previous studies (Bergmann et al., 2017; Eo et al., 2018; Katija et al., 2017). Also, the large MPs become small MPs periodically due to breakdown and other environmental processes (Andrady, 2011). Further to that, it has been speculated that the small MPs of different shape-sizes are of specific concern due to its higher abundances and potential harmful impacts (de Sa et al., 2018). On the other hand, the small MPs sink more easily than the large ones do (Katija et al., 2017; Ryan, 2015). Besides, small MPs creates the higher probability of ingestion by the marine organisms than the large MPs (Jovanovic, 2017; Guven et al., 2017; Zheng et al., 2020; Egbeocha et al., 2018) as well as the higher proportions of small MPs were detected in aquatic organisms as reported in the field studies Tanaka and Takada, 2016; Lusher et al., 2016; de Sa et al., 2018; Jovanovic, 2017; Critchell and Hoogenboom, 2018. Lei et al. 2018 stated that the smaller the MP particle size represents the greater hazards. In addition, MPs contain hazardous chemicals derived from additives and plasticizers in their formulation products, adsorb persisting organic pollutants, heavy metals and hydrophobic contaminates, and thus, enhance toxins bioaccumulations. Small MPs particle sizes of different shapes adds higher surface areas to sorb contaminants (Yu et al., 2019; Antunes et al., 2013). Thus, MPs present a chemical hazard in marine ecosystems in which small MPs are more dangerous potential (Tanaka and Takada, 2016; Chae and An, 2017). Hence, the findings in this study indicated that the MPs shape-size types might be of harmful potential while the small MPs are of more harmful potential for these SIS and SJ marine aquatic systems. However, robust ecological risk assessment studies are required furtherly to understand the environmentally harmful abundances and distribution, ecotoxicological effects and impacts of each MPs shape-size types over the reported abundances in this study for these marine aquatic systems.

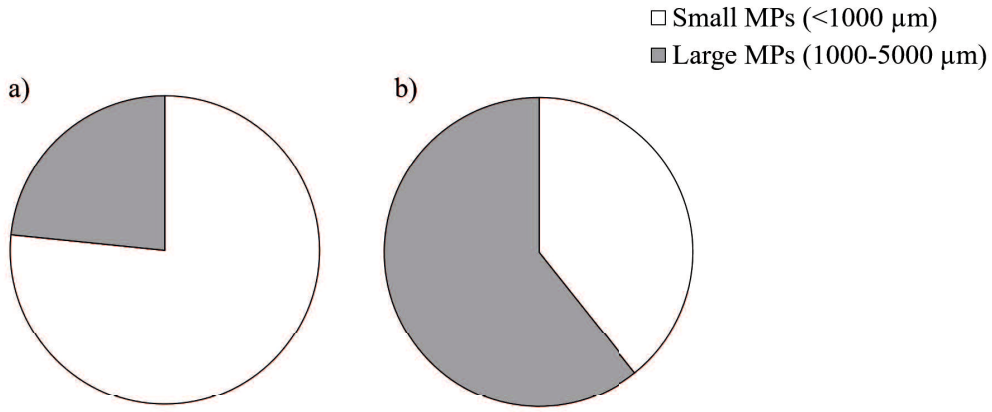

Fig. 2.4 Size based MPs proportions and distributions in the sea surface sediments and water of the SIS and SJ areas (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water'). All the size ranges are in 'μm'.

On the other hand, different types of MP shapes-sizes and concentrations based ecotoxicological studies were monitored across several groups of organisms in the laboratory studies (de Sa et al., 2018). MPs particles (96 h; 420–500 μm; 100 particles L^{-1}) ingestion demonstrated reduced predatory performance and efficiency in *Pomatoschistus microps* (de Sa et al., 2015). MP particles (240 h and 1008 h; 10–27 μm; 0–10^8 particles L^{-1}) and fibers (240 h and 1008 h; 20–75 μm; 0–9 × 10^4 particles L^{-1}) affected growth and

reproduction of a large crustacean, the amphipod *Hyalella Azteca* (Au et al., 2015). Avio et al. 2015 documented enzyme alteration effects by MPs exposure (168 h; <100 μm; 2 × 10^3 mg L^{-1}) in the *Mytilus galloprovincialis*. Zhang et al. 2018 assessed ecotoxicological effects based on the following published researches– MP fibers (1–1000 μm; 1 x 10^3 particles L^{-1}) affects reproduction, physical damages (carapace and antenna deformities), survival and growth of *Ceriodaphnia dubia* at the acute (48 h) and chronic (8 d) exposure (Ziajahromi et al., 2017); MP particles (30 d; 70–88 μm; 403 particles L^{-1}) affected predatory performance, digestion and energy production of *Symphysodon aequifasciatus* (Wen et al., 2018) and histopathological alterations of *Clarias gariepinus* by MP fragments (96 h; <100 μm; 700 particles L^{-1} (Karami et al., 2016). From these laboratory studies, it can be noted that environmentally relevant concentrations including the reported abundances in this study as well as higher MP concentrations than reported abundances from many other field studies on the marine organisms, surface water and sediment were found to cause ecotoxicological effects in the aquatic organisms (de Sa et al., 2018; Burns and Boxall, 2018). On the other hand, there are significant mismatches between the commonly found MP shape-size types reported in field studies and those used in laboratory studies which demonstrated a clear research gap de Sa et al., 2018. Thus, this demands a need to know the harmful abundances and distribution of MPs and understand their toxicity mechanisms to aquatic organisms in accordance with environmentally relevant concentrations and types of MPs to conclude the ecotoxicological effects (de Sa et al., 2018; Burns and Boxall, 2018). Hence, overall MP harmful abundances and ecotoxicological impacts understandings on aquatic ecosystems, food web and human health are not yet conclusive.

2.3.3.3. Shape-color

The extracted microplastics were grouped into visually obvious colors (transparent, white, green, blue, yellow, red and grey). The results showed that transparent (26.38%) MPs were predominant followed by green (22.79%) >blue (21.55%) >grey (19.85%) >white (7.15%) >yellow (1.16%) >red (1.12%) of totally identified MPs from the sediments. On the other hand, from the water samples, transparent (38.35%) >red (29.72%) >blue (23.16%) >green (8.84%) MPs were extracted (Table S2.1). Both the SJ and SIS areas had various colorful MPs in the sea surface sediments and water (Fig. 2.5). The transparent and colorful MPs particles abundances were found in many other studies.

Industries use a great variety of colors during plastics production. Also, environmental weathering and degradation processes may occur in the environment and thus, colors might be affected. Therefore, although colors might not be the permanent and rigid identifying characteristics, there exists environmental importance of this character (Stolte et al., 2015). The large variety of shape-color characteristics might indicate that the MPs particles were originated from variety of sources. For example, the mass uses of transparent and colorful polyethylene bags for packaging purposes can be the source of transparent and colorful films (Stolte et al., 2015). The wide uses of large variety of colorful plastics in various purposes might lead to various colored MPs and indicate the variety of MPs occurring sources in these SIS and SJ areas. Besides, the large variety of colors for MPs particles are similar to some natural marine foods. Therefore, these MPs may confuse natural prey and predator behaviors in the aquatic systems. Mistaken ingestion of MPs by marine organisms might happen (Wright et al., 2013) Thus, the variety of shape-color MPs in the SIS and SJ were indicative to be potentially harmful for marine organisms. Besides, color has also been recognized as a good indicator of residence time at the ocean surface and degree of weathering (Jang et al., 2017). The degree of MPs particles discoloration, being faded or darkening happens largely

due to the extent of surface oxidation, aging or degradation (Stolte et al., 2015; Jang et al., 2017; Prata et al., 2020; Gewert et al., 2015). In this study, both fair, bright and fresh as well as dull and faded MPs were found. We speculated that the dull and faded MPs colors might be transported across the both SIS and SJ seas and underwent various aging processes, e.g. weathering and degradation over a long residence time span while the fresh and bright colors might be the indicators of short residence time span in the environments, low level surface oxidation, weathering and degradation, and thus discoloration didn't appear yet. In addition, we also used shape-color based characteristics together for categorization to identify the polymers (Figure S2.2 and Table S2.2).

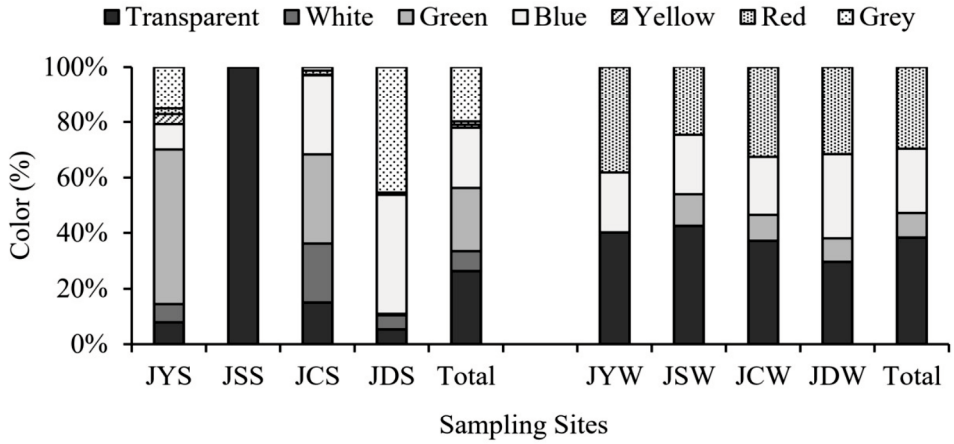

Fig. 2.5 Color based MPs proportions and distributions in the sea surface sediments and water in the SIS and SJ areas (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water').

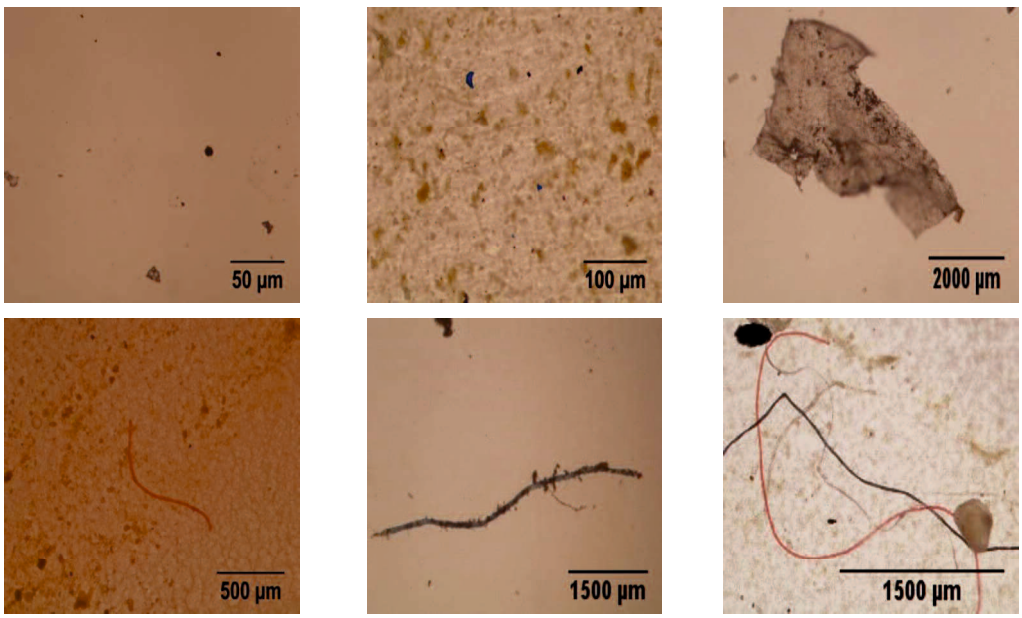

Fig. 2.6 Microscopic view of different types of MPs extracted from the sea surface sediments and water in the SIS and SJ areas.

2.3.3.4. Polymers

The ATR-FTIR analysis revealed five different polymers were following– polyethylene (PE), polyvinyl alcohol (PVA), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS). All the ATR-FTIR spectrum for these identified polymers are given in Fig. S2.3. MPs shape and color-based characterization showed that transparent, white and yellow fragments, and films were mainly PE. All the fibers and green fragments were mainly PET and PE. PVA was identified from blue fragments, green and blue colored films. Grey and dark blue fragments and white films were PP. The red fragment particles were identified as PS (Table S2.2).

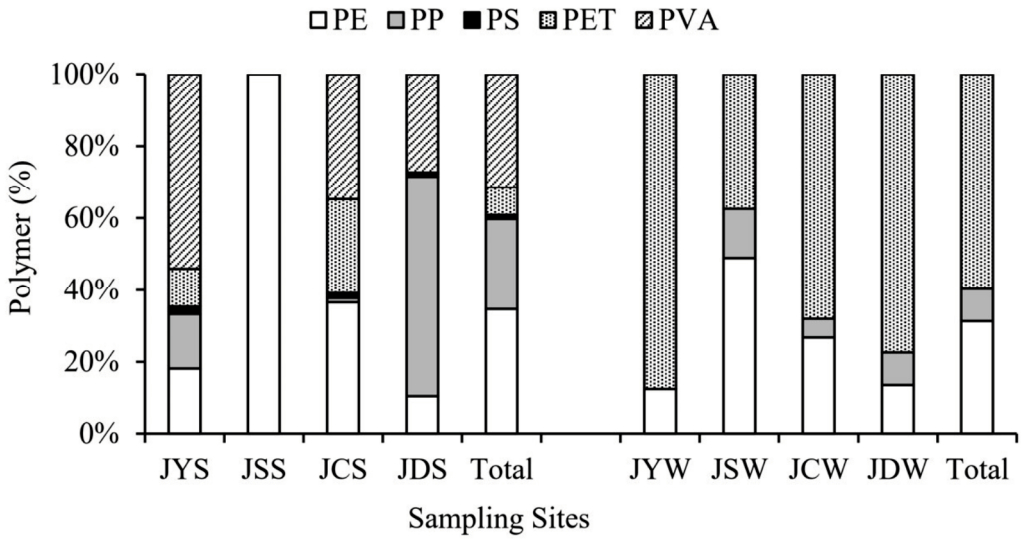

Fig. 2.7 Proportion of different polymeric compounds of totally extracted MPs from sea surface sediments and water and their distributions in the SIS and SJ (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water').

The results demonstrated that PE accounted for 34.69% as the predominant polymer in the sea surface sediments followed by PVA (31.52%), PP (25.03%), PET (7.65%), and PS (1.12%). From the environmental distribution point of view, PE, PVA, and PET were abundant in the SIS areas whereas PP and PVA were predominant in the SJ sediments. Surprisingly PE accounted for 100% in the Shiratsuchi Beach sediments, PVA was prevalent in the Yamaguchi Bay and Chofu Beach of SIS areas. On the contrary, PET (59.71%) predominated the sea surface water followed by PE (31.33%) and PP (8.97%). Yamaguchi Bay had the highest proportion (87.63%) of PET fibers and Shiratsuchi Beach had the highest proportion (48.92%) of PE fibers and fragments of SIS areas. On the other hand, the polymeric compound proportions were following PET (77.42%) >PE (13.55%) >PP (9.03%) in the Doigahama Beach area of SJ. No noticeable compositional differences were found for the surface water in the both seas (Fig. 2.7). However, the differences in polymeric compounds distributions in the sediments of the both SIS and SJ areas might indicate the occurrences of MPs pollution from different sources. Further to that, higher PVA abundance in the sediments in this study indicated the abundance of an uncommon polymeric compound in these marine areas than many other studies (Table 2.2 and 2.3).

PE (0.92–0.97 g/cm^3) and PP (0.90–0.91 g/cm^3) are the low-density polymeric compounds than seawater (1.02 g/cm^3) (Frias et al., 2018). They are most commonly reported polymeric compounds from the sea surface sediments and water samples (Table 2.2 and 2.3). Surprisingly, a far higher abundance of PE and PP MPs in the sediments compared with surface water was found in the Tokyo Bay (Matsuguma et al., 2017). PET (1.37 g/cm^3) is the high-density thermoplastic polymer resin of the polyester. PET prevalence in sea surface sediments and water was found in many other studies (Bergmann et al., 2017). PS (0.01–1.06 g/cm^3) higher abundances have also been reported in marine sediments (Jang et al., 2017). PVA (1.19 g/cm^3) is persistent and assumed to be environmentally harmful (Julinova et al., 2018). More often, the marine sediments and water had very higher concentrations of these identified polymers (Table 2.2 and 2.3). Besides, such polymers are long persistent that might reflect long-term pollution in the marine systems (GESAMP, 2015; Smith et al., 2018; Nel and Froneman, 2015). Moreover, numerous ecotoxicological effects on marine organisms of different MP polymer types have been reported. MP induced neurotoxicity and lipid oxidative damage was found in marine fish *Dicentrarchus labrax* (Barboza et al., 2018). Predatory efficiency reduction in goby fishe, *Pomatoschistus microps*, reduced growth and reproduction in amphipod, *Hyalella azteca* were evident by PE and PP (Au et al., 2015) PE and PS MPs induced oxidative stress, neurotoxicity, changes in gene expression and immune response, alterations in enzyme, and genotoxicity were found by in the marine mussel, *Mytilus galloprovincialis* (Avio et al., 2015). PS MPs exposure revealed upregulation of genes involved in the nervous and visual larvae, changes in immune system, enriched toxicity pathways for lipid metabolism and oxidative stress in zebrafish, *Danio rerio* (Chen et al., 2017; Veneman et al., 2017), decrease in survival and fecundity of copepod, *Calanus helgolandicus* (Cole et al., 2015), neurotoxicity and oxidative stress in *Amphibalanus Amphitrite (Gambardella et al., 2017),* oxidative stress as well as *affecting* growth rate and fecundity in *Paracyclopina nana (Jeong et al., 2017)*, neurotoxicity and genotoxicity in mollusk, *Scrobicularia plana* (Ribeiro et al., 2017), decrease in growth rate and fecundity in rotifers, *Brachionus koreanus* (Jeong et al., 2016). Studies reported PET toxicological effects such as mortality, productivity, population sizes and gene expression in copepod, *Parvocalanus crassirostris* (Heindler et al., 2017). Overall, MPs caused numerous negative impacts on marine aquatic organisms have been evident by these identified polymers– PE, PP, PS and PET (de Sa et al., 2018). PVA toxicity is not well known. However, a high degree of polymerization may cause harm to the human organism (Julinova et al., 2018). In addition to polymeric composition induced ecotoxicological effects, these polymers contain additives, adsorb POPs, heavy metals and hydrophobic contaminants which are bio accumulative (e.g., toxic flame retardant hexabromocyclododecanes [HBCDs], phthalates) (de Sa et al., 2018; Chae and An, 2017; Jang et al., 2017; Burns and Boxall, 2018). In such context, these identified polymers might create long-term pollution, enhanced chemical toxicity and harm to the marine aquatic organisms in these SIS and SJ marine ecosystems.

2.3.4. Occurrences Potentials of Microplastic Pollution in the SIS and SJ

All the identified polymers are man-made for our modern daily life uses. They are commonly used in industries, commercials, domestics and daily life, agriculture etc. (Plastic Europe, 2018). For example– the bulk of common thermoplastics manufactured (PE, PP) are used in packaging products., have a relatively short useful lifetime and ended up in the waste and litter streams rapidly (GESAMP, 2015). PET fibers are most commonly found from textiles and clothing (Falco et al., 2019; Napper and Thompson, 2016). PS comes from light industries, such as daily decoration, coloring, lighting instructions and packaging (Wen et al., 2018). PVA applications are mainly found in industrial, commercial, medical, and

food sectors (Julinova et al., 2018). Moreover, the above stated polymeric items are mostly produced and consumed globally. The Japan Plastics Industry Federation (JPIF) statistical report of 2019 revealed that large amounts of plastics materials (PE, PP, PS, PET, and PVA productions are following– 2.47, 2.36, 0.78, 0.40, and 0.21 million tons respectively) were produced in the year of 2018. On the other hand, Plastic Europe 2018 reported that PE, PP, PS and PET constituted 63.2% of total produced and consumed plastics (Plastic Europe, 2018). Thus, the polymers indicated that plastics production and consumption through anthropogenic activities can be easily speculated as the possibly main primary causes and sources in these studied regional marine environments as well as all over the globe.

Fig. 2.8 PET bottles from foreign countries in the Doigahama beach area of SJ (Source: Field survey, 2018).

Also, the MP abundances and distributions are also closely related to other environmental processes and factors such as plastics breakdown (weathering, UV exposure, degradation, and physical stress), MPs transportations and deposition Cole ta al., 2011; Andrady et al., 2011; Auta et al., 2017; GESAMP 2015; Gewert et al., 2015. Studies speculated that the ocean currents and meteorological conditions might accumulate MPs through long-range transportations. The SJ has connections with Asian Seas such as China Yellow Sea, East China Sea, South Korea coastlines, China South Sea Isobe et al., 2014 & 2015, Su et al., 2016; Iwasaki et al., 2017; Zhang, 2017. Moreover, the SJ area of Yamaguchi prefecture is transitional to other country's (Korea and China) marine areas. More interestingly, we found the PET bottles with Chinese and Korean characters during field survey in the SJ area (Fig. 2.8). Besides, the 'Waste, recycling measures section' of the Yamaguchi Prefecture local government conducted a plastic garbage collection programme from the Japan-Republic of Korea (ROK) coasts of the SJ areas on 30th May 2019. About 30% of the plastic PET bottles were from Japan and 70% were from foreign countries in which 48.3% were from Korea and 19.2% from China. In addition to that, Iwasaki et al. 2017 demonstrated that the MPs and mesoplastics were transported and spread into the SJ coastal areas by the northeastward 'Tsushima Current' from other areas (Iwasaki et al., 2017). The current flows from the East China Sea through the Korea/Tsushima strait along the west coast of 'Kyushu and Honshu Island, Japan' representing the inclusion of this study area 'the SJ surrounding Doigahama coasts (JD) of Yamaguchi Prefecture' (Iwasaki et al., 2017; Gallagher et al., 2015). The same study explained that polypropylene (PP; 0.85–0.9 g cm−3) might be the dominant polymer than polyethylene (PE; 0.91–0.97 g cm−3) in SJ due to low-density and being carried out by the current. In our results, we observed foreign plastic waste bottles were of China and Korea origin as well as PP dominance in the SJ which corroborated Iwasaki et al., 2017. Overall, both plastics and MPs originated from the other

areas might enter the SJ through long range transportations. However, this speculation of higher PP dominance due to long-range transportation from foreign areas in SJ beach area might be hindered by the limitation as the samples in this study were taken at the beach, which might also be affected by beach sediment or river water flowing from Japan land. This demands for future investigation of MPs released by the Japanese rivers into these SJS and SJ beaches areas. On the other hand, the SIS mainly lies inside the geographic proximity of Japan. Isobe et al. 2014 revealed that the transport and spread of MPs and mesoplastics occurred in the near-shore and offshore areas in the SIS marine aquatic environments. This indicated that the MPs and mesoplastics occurrences in these SIS areas are likely originated from the anthropogenic activities on Japan land Isobe et al., 2014. Thus, overall, we speculated that SJ area might receive MPs originated on the other land or sea areas by long-range transportations as well as domestic Japan sources while the SIS might receive MPs from the domestic Japan land sources. However, source tracking of plastics and as well as the MPs, their sources, transportation pathways and fates are recommended to investigate further.

2.4. Conclusions

The present study represented the first MP pollution report in the SIS and SJ surrounded Yamaguchi prefecture areas, Japan. Similar level of MP pollution could be speculated in the both SIS and SJ areas. Overall, higher sea surface water MP abundances and medium to high-level abundances in the sediments revealed medium to high-level MP pollution than other studies. In the context of sea surface sediments, small MPs (<1000 μm) fragments and films predominated the SIS areas while mainly small MPs fragments (<1000 μm) predominated the SJ area. Large MPs (1000–5000 μm) fibers predominated the sea surface water similarly in the both sea areas. Both the SJ and SIS areas had various colorful MPs in the sea surface sediments and water. PE, PP and PVA were the major polymers in the sea surface sediments. PE and PVA predominated the SIS while PP was predominant in the SJ sediments. Overall, PET and PE predominated sea surface water similarly both in the SIS and SJ areas. The different MP characters (shapes-sizes-colors-polymers) in the sea surface sediments and water of SIS and SJ areas might be indicative to the variety of causes and sources of MP pollution, potential ecotoxicological effects and long-term pollution in these marine systems. Anthropogenic activities as well as environmental factors could be the possible main sources of MP pollution in the both seas. We speculated that the SIS areas might have MPs from Japan origin while the SJ area might have MPs from both the Japan as well as other country origins. Overall, the MP pollution in the SIS and SJ areas might be alarming as well as of paramount importance towards marine environmental protection and sustainability. Further investigations are required for MP sources, transportation pathways and fates in these marine environments.

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Supplementary Materials

Table S2.1 MPs characteristics and their proportions

Characteristics	Sediment (%)	Water (%)
Sizes (µm)		
50-250	45.15%	26.91%
250-500	16.92%	03.55%
500-1000	14.50%	08.84%
1000-2000	15.20%	24.50%
2000-5000	08.23%	36.21%
Shape (types)		
Fragment	62.51%	18.81%
Film	34.51%	10.91%
Fiber	02.68%	70.28%
Granule	0.30%	
Color (types)		
Transparent	26.38%	38.35%
White	07.15%	--
Green	22.79%	08.84%
Blue	21.55%	23.16%
Yellow	01.16%	--
Red	01.12%	29.72%
Grey	19.85%	--

Table S2.2 Shape-color based MPs categorization

	Transparent	White	Green	Blue	Dark Blue	Yellow	Red	Grey
Fragment	PE	PE	PET	PVA	PP	PE	PS	PP
Film	PE	PE, PP	PVA	PVA	--	--	--	PP
Granules	PE	PE	PE	PE	--	--	--	PP
Fiber	PE, PET	--	PET	PET	--	--	PET	--

Table S2.3 Shape based correlation (Pearson Correlation Test) tables between sediment and water

a) Correlations of Fragment shape MPs between Sediment and Water

		FragmentsS	FragmentsW
FragmentsS	Pearson Correlation	1	.040
	Sig. (2-tailed)		.878
	N	31	17
FragmentsW	Pearson Correlation	.040	1
	Sig. (2-tailed)	.878	
	N	17	17

b) Correlations of Film shape MPs between Sediment and Water

		FilmS	FilmW
FilmS	Pearson Correlation	1	-.382
	Sig. (2-tailed)		.130
	N	31	17
FilmW	Pearson Correlation	-.382	1
	Sig. (2-tailed)	.130	
	N	17	17

c) Correlations of Fiber shape MPs between Sediment and Water

		FiberS	FiberW
FiberS	Pearson Correlation	1	.173
	Sig. (2-tailed)		.506
	N	31	17
FiberW	Pearson Correlation	.173	1
	Sig. (2-tailed)	.506	
	N	17	17

Table S2.4 Size based correlation (Pearson Correlation Test) tables between sediment and water (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water')

a) Correlations of '50-250 μm' size MPs between Sediment and Water

		S250	W250
S250	Pearson Correlation	1	-.478
	Sig. (2-tailed)		.098
	N	31	17
W250	Pearson Correlation	.403	1
	Sig. (2-tailed)	.098	
	N	17	17

b) Correlations of '250-500 μm' size MPs between Sediment and Water

		S500	W500
S500	Pearson Correlation	1	.109
	Sig. (2-tailed)		.677
	N	31	17
W500	Pearson Correlation	.109	1
	Sig. (2-tailed)	.677	
	N	17	17

c) Correlations of '500-1000 μm' size MPs between Sediment and Water

		S1000	W1000
S1000	Pearson Correlation	1	-.161
	Sig. (2-tailed)		.536
	N	31	17
W1000	Pearson Correlation	-.161	1
	Sig. (2-tailed)	.536	
	N	17	17

Table S2.4 Size based correlation (Pearson Correlation Test) tables between sediment and water (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water') (Continued)

d) Correlations of '1000-2000 μm' size MPs between Sediment and Water

		S2000	W2000
S2000	Pearson Correlation	1	-.194
	Sig. (2-tailed)		.456
	N	31	17
W2000	Pearson Correlation	-.194	1
	Sig. (2-tailed)	.456	
	N	17	17

e) Correlations of '2000-5000 μm' size MPs between Sediment and Water

		S5000	W5000
S5000	Pearson Correlation	1	-.342
	Sig. (2-tailed)		.179
	N	31	17
W5000	Pearson Correlation	-.342	1
	Sig. (2-tailed)	.179	
	N	17	17

Supplementary figures

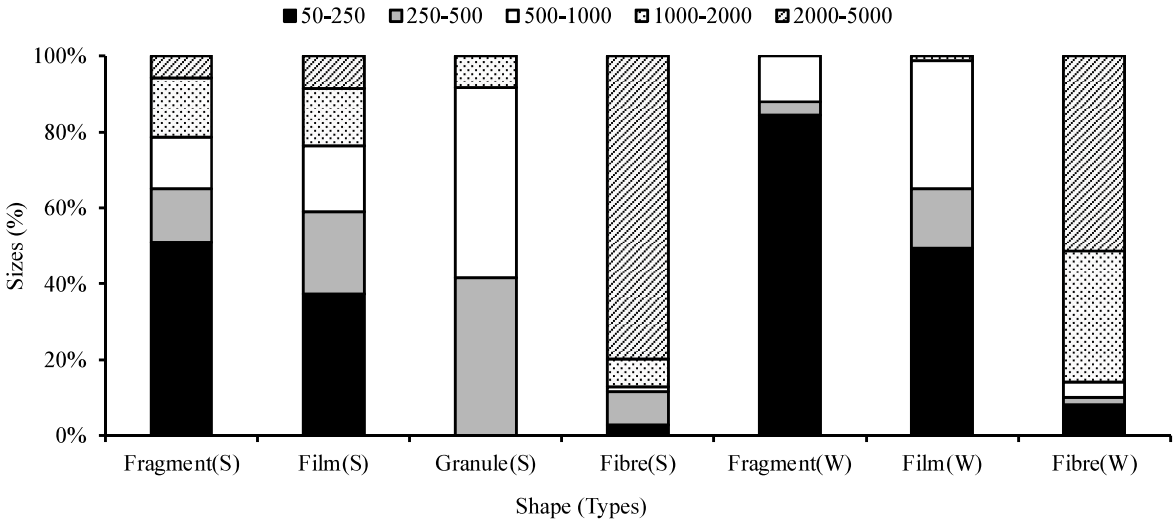


Fig. S2.1 Shape (types)-sizes (μm) categories-based MPs proportions in the sea surface sediments and water (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water'). All the sizes are in 'μm'.

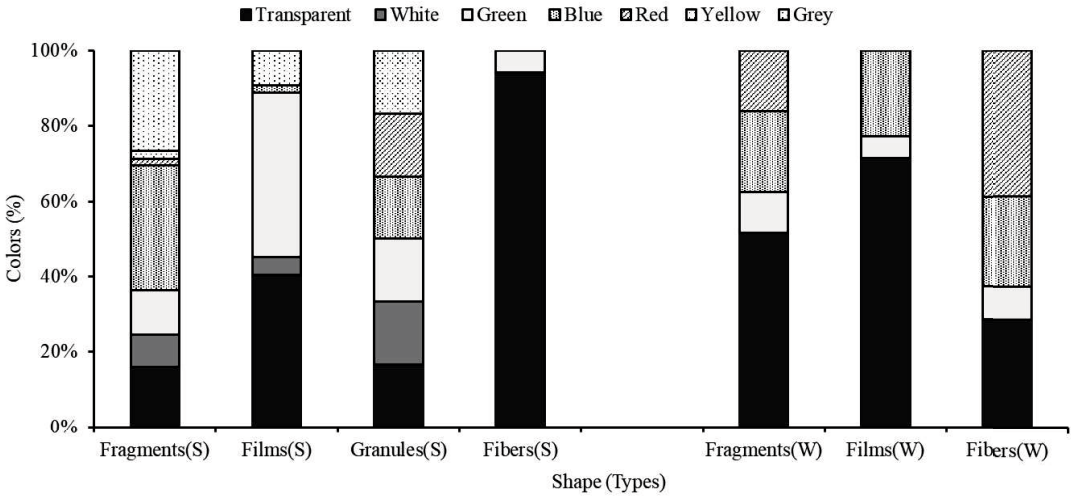
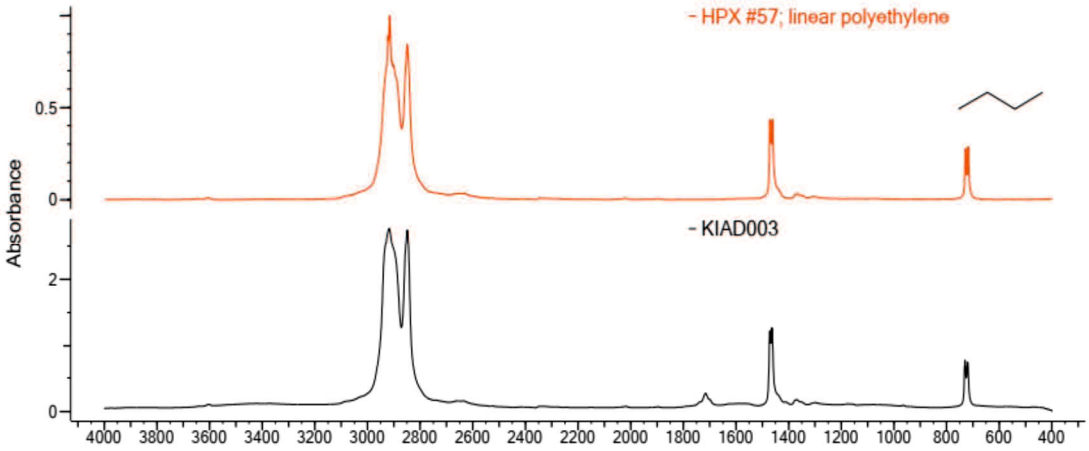
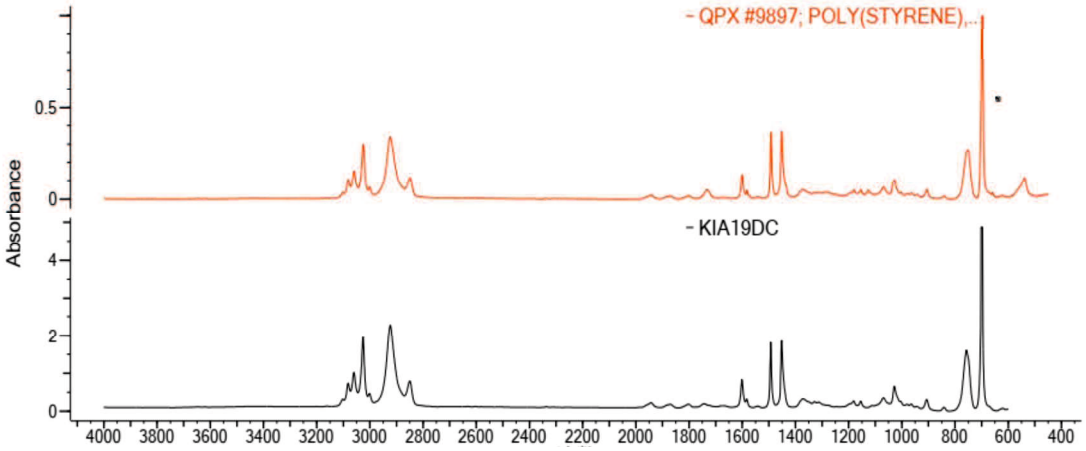


Fig. S2.2 Shape-color based MPs proportions in the sea surface sediments and water (N. B. 'S' stands for 'Sediment' and 'W' stands for 'Water').

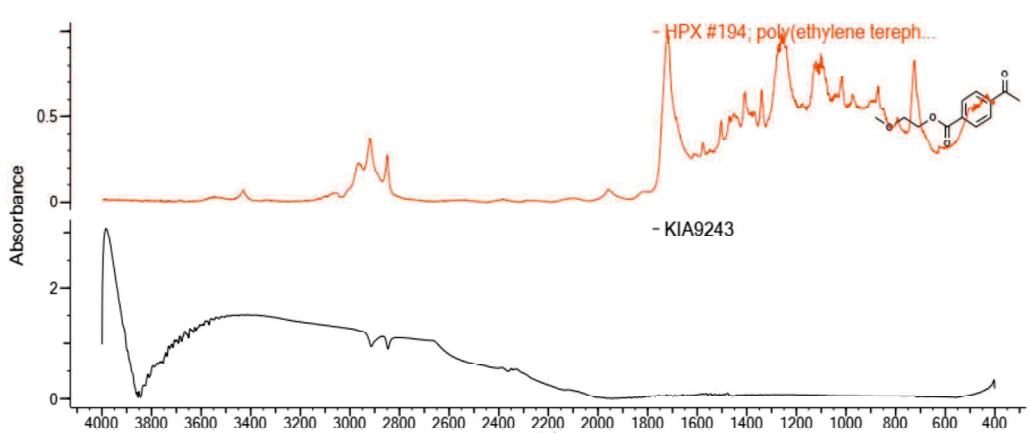
A


- HPX #57; linear polyethylene
- KIAD003
Absorbance
0.5
0
2
0
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400

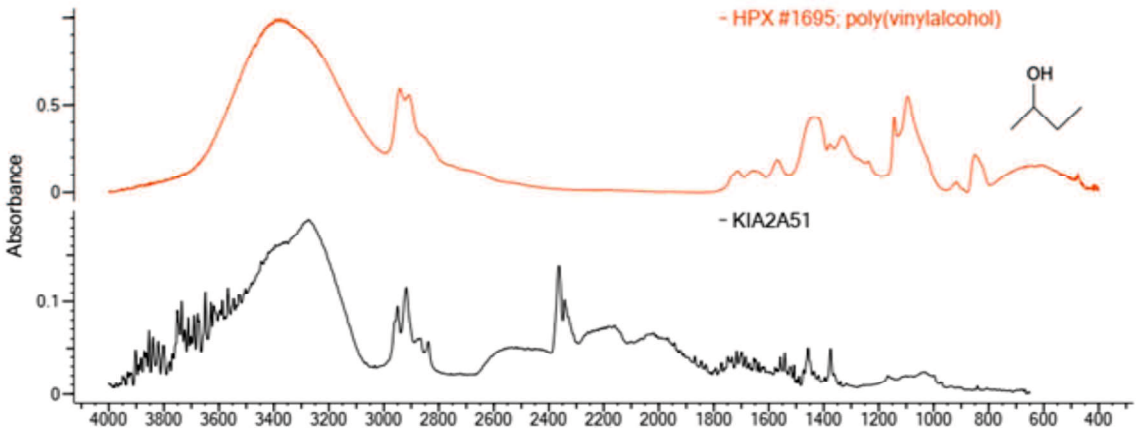
B


- QPX #9897; POLY(STYRENE),...
- KIA19DC
Absorbance
0.5
0
4
2
0
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400

C


- HPX #194; poly(ethylene tereph...
- KIA9243
Absorbance
0.5
0
2
0
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400

D



E

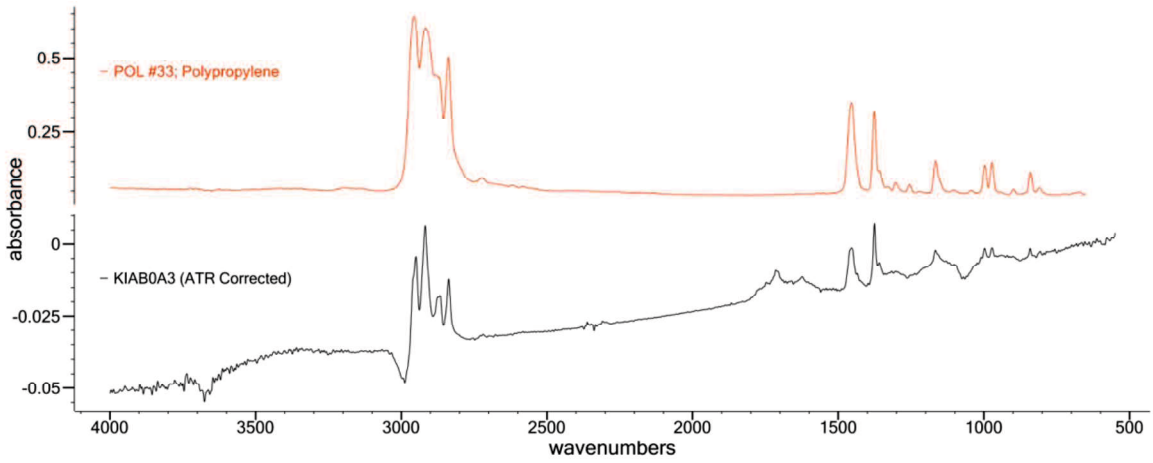


Fig. S2.3 ATR-FTIR Spectra for- A) Polyethylene (PE), B) Polystyrene (PS), C) Polyethylene Terephthalate (PET), D) Polyvinyl Alcohol (PVA), and E) Polypropylene (PP)

Chapter 3

Assessing Small-Scale Freshwater Microplastic Pollution, Land-use, Source-to-Sink Conduits, and Ecological Risks: Perspectives from Japanese Rivers Polluted with Microplastics

This chapter assessed MP pollution in the surface water of the small-scale Japanese rivers, estimated the river-to-marine emission as the sources-to-sink conduits, assessed ecological risks and identified the Japan land-sourced MPs. Overall, this study filled the preliminary knowledge gaps regarding the freshwater MPs pollution in Japan, influences of rivers to cause SIS and SJ marine pollution by emitting Japan land-sourced MPs as well as understanding the pollution ecological risks with a focus of stated knowledge gaps identified in the previous study (Chapter 2) and in the Introduction part (Chapter 1).

Abstract

Rivers are vital for understanding freshwater microplastic pollution, along with the conduits from land-sources to marine-sinks. In this study, we investigated microplastics in the small-scale Awano and Ayaragi rivers, which flow into the Sea of Japan (SJ), and the Asa and Majime rivers, which flow into the Seto Inland Sea (SIS) in Yamaguchi Prefecture, Japan. Surface water samples were collected from 29 stations. Filtration, wet peroxidation, and density separation methods were employed to extract microplastics. Polymers were identified via attenuated total reflectance-Fourier transform infrared spectroscopy. Microplastic abundances and comparisons among them revealed that the small-scale Japanese rivers were more polluted than others around the world. Characterization demonstrated that small microplastics (<1,000 μm) in size, fibers and fragments in shape and the polymers— polyethylene, polypropylene, vinylon, polyethylene terephthalate, and polystyrene were dominant. Both point and non-point sources could release microplastics into the riverine environments. The small-scale rivers emitted substantially higher quantities of microplastics (0.4–154.27 billions/day and 0.01–17.55 tons/day) into the SJ and SIS environments than larger rivers in other regions. The pollution load index indicated that all of the river stations were polluted with microplastics. An assessment of the polymeric and pollution risks revealed variably low to high risks. The higher were the abundances of microplastics and toxic polymers, the higher were the pollution level and risks. The sites at high risk of pollution were regarded as hotspots. Risk-zones and hotspots identification indicated that both point and non-point sources might affect posing high risks. Moreover, the pollution characteristics indicated that pollutants posed serious ecotoxicological threats to the rivers and their downstream environments. This study provides new insights into riverine microplastic pollution and revealed small-scale rivers to be prominent conduits of sources-to-sinks. Our risk assessments also provided a baseline for future comprehensive assessments and practical approaches to pollution management.

Keywords: Riverine microplastic pollution, pollution load index, ecological risk assessment, conduits, point source, non-point source

3.1. Introduction

Plastics, which are composed of synthetic polymers, have occupied all spheres of modern daily life. There has been a continually increasing trend in plastic production and consumption since the mid-20th century. In 2018, 359 million tons of plastics were produced globally, with Asia accounting for 51% of all plastics worldwide (China: 30%; Japan: 4%; other Asian nations: 17%) (Plastics Europe, 2019). The application and use of plastics are ubiquitous, with numerous benefits and advantages to daily life, society, and the economy (Andrady and Neal, 2009; Plastics Europe, 2019). However, the impacts of plastics on the environment have also become increasingly apparent. Aquatic environments are polluted with plastics worldwide (GESAMP, 2016; van Emmerik and Schwarz, 2020).

Microplastics (MPs) — micron-sized plastic particles (~5000 μm) — a class of plastic pollutants, are regarded as emerging pollution threats (Frias et al., 2019; Lambert and Wagner, 2018). The abundances, distributions, types, and characteristics (i.e., shape, size, color, and polymer type) of marine MPs pollution, and the potential ecotoxicological threats posed by MPs have been the focus of research and are globally well-reported (Andrady, 2011; Cole et al., 2011; Auta et al., 2017; Peng et al., 2020). However, the existing knowledge on freshwater MPs pollution is relatively lacking, though it is increasingly receiving scientific attention. Despite the recent findings of higher MP abundances and speculated threats in freshwater environments, the information available on the abundance, distribution, characteristics, hotspots, risks, fates of MPs in riverine environments remains inadequate (Li et al., 2018; Dris et al., 2015; Bletter et al., 2018; Horton et al., 2017).

MPs are sourced on land from the manufacturing of plastic particles, including personal care products, agricultural fertilizers, household and industrial detergents, cleaning products, and paints (primary MPs), and from the fragmentation of larger plastics (secondary MPs) under different environmental conditions (e.g., exposure to sunlight and oxidants, mechanical abrasion, weathering, degradation, etc.) (Cole et al., 2011; Andrady, 2011; Jambeck et al., 2015; Gewert et al., 2015; Scudo et al., 2017). Riverine and marine systems receive MPs from land-based point and non-point sources (Jambeck et al., 2015; Siegfried et al., 2017; Kataoka et al., 2019; Baldwin et al., 2016). Several studies have indicated that the land-use characteristics of point sources (i.e., population density, urban and residential areas, domestic sewage, wastewater treatment plants (WWTPs), industries, etc.) affect the occurrence of MPs pollution (Kataoka et al., 2019; Murphy et al., 2016; Lechner and Ramler, 2015). Several other studies have indicated that they have no significant impact (Nel et al., 2017; Klein et al., 2015; Vaughan et al., 2017). Land use related to non-point pollution sources (e.g., agricultural, atmospheric transportation, fallouts and deposition etc.) might also be major contributors of MPs in the aquatic environments (Dris et al., 2016; Baldwin et al., 2016; Allen et al., 2019; Huang et al., 2020; Ouyang et al., 2020; Qiu et al., 2020; Dris et al., 2018). However, little is certain regarding the influences of land-use over the point and non-point sources of MP pollution in the context of riverine environments (Kataoka et al., 2019; Siegfried et al., 2017).

Marine environments are thought to be the largest sink of land-sourced MPs (Jambeck et al., 2015), while rivers are plastic pollution hotspots and serve as the major conduits of land-sourced MPs emissions into the marine realm (Horton and Dixon, 2018; Jambeck et al., 2015; Lebreton et al., 2017; Schmidt et al., 2017; Bowmer and Kershaw, 2010). It has been estimated that ~80% of plastics in the sea are sourced from the land and emitted by rivers (Jambeck et al., 2015; Bowmer and Kershaw, 2010). In modeling studies,

Lebreton et al. (2017) estimated 1.15 and 2.41 million tons of MPs enter the ocean via rivers. Schimdt et al. (2017) predicted the export of between 5×10^{-4} and 6.3×10^{3} tons of MPs per day by the largest river catchments of the world. Lechner et al. (2014) estimated the micro- and meso-plastic litter inputs to be 4.2 tons per day from the Danube River into the Black Sea. Thus, river-to-marine MPs emissions are critical for understanding the transformation, fate, and loadings of plastic pollution from land sources to marine sinks. To date, studies on the MPs emissions from rivers to oceans have been limited (Horton et al., 2017; Hurley et al., 2018). MPs pollution in small-scale freshwater bodies is more serious than in coastal waters (Hu et al., 2018; Luo et al., 2019), yet the MPs in small-scale rivers and their quantitative MPs emissions remain unknown.

The Sea of Japan (SJ) and the Seto Inland Sea (SIS) are noted as MP pollution hotspots in Japan (Isobe et al., 2015). In a previous MP pollution study, Kabir et al. (2020a) suggested moderate to high levels of MP pollution along the SJ and SIS coasts in Yamaguchi Prefecture. Differences in the characteristics of MPs were observed between the SIS and SJ. Moreover, foreign plastic bottle waste has been found on the SJ coast. Overall, the results of this past study suggest that the SJ coast is affected by MPs and plastic waste originated from Japan land-sources, as well as other areas (Kabir et al., 2020a). The occurrence of foreign plastics and MPs in the SJ might be due to long-range transportation (Iwasaki et al., 2017). The findings emphasized the importance of studying Japanese inland river MPs to understand MP pollution originating from land sources in Japan, as well as their characteristics. On the contrary, information on riverine MP pollution is very limited in Japan. Thus, the study of MP pollution in Japan's inland rivers may provide valuable new insights about river freshwater pollution and land-sourced MPs. Besides, estimates of fluvial MPs emissions to the receiving SIS and SJ environments will also reveal the influences of the land sources and river conduits responsible for SJ and SIS pollution (i.e., source-to-sink). More broadly, such information will aid in the development of MP pollution control and management approaches in Japan.

MPs comprise a long-lived and diverse suite of pollutants that vary in shape, size, color, polymer type, plasticizer, stabilizer, colorant, and other attributes. They are also able to adsorb other eco-toxins, including persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals, and easily spread via long-range transport in aquatic environments. Thus, MPs may be transferred through food webs and their exposure to all biotic and abiotic matrices is unavoidable (Rochman et al., 2019; Yu et al., 2019; Gallo et al., 2018; Oliveira et al., 2019; Carbery et al., 2018; Hale et al., 2020). Lithner et al. (2011) classified plastic polymers as carcinogenic and mutagenic to humans, as well as highly toxic to aquatic life, with long-lasting effects. Consequently, the MP pollution poses greater risks to the environment, human health, and hinders global environmental protection and sustainability (Rochman et al., 2015; Galloway, 2015; Koelmans et al., 2017; Wright and Kelly, 2017; Eerkes-Medrano et al., 2015). Despite the wide abundance of MPs in aquatic environments, existing knowledge on pollution risks remains limited (Koelmans et al., 2017). Hence, the development of a pollution load index, as well as polymeric and pollution ecological risk assessments are necessary for the understanding MP pollution and its hotspots, and to further develop policies for pollution control and management.

In this study, we explore the MP pollution in selected SJ- and SIS-flowing rivers in Yamaguchi Prefecture, Japan. We also extend the study of Kabir et al. (2020b) to develop pollution insights based on an MP pollution load index and risk assessments. Overall, our objectives were to: (1) investigate small-

scale riverine MP pollution and identify the potential land-use sources affecting the occurrence of MPs; (2) estimate the MP loadings of the rivers into the SJ and SIS; (3) develop MP pollution insights through measured pollution load indices, and ecological risk assessments, and identify pollution hotspots to facilitate environmental monitoring and pollution management. This study appears to be the first comprehensive assessment of small-scale rivers MPs pollution, Japan land-sourced MPs loadings into the SIS and SJ marine sinks by the rivers as source-to-sink conduits and the MP pollution risks in the riverine environments.

3.2. Materials and Methods

3.2.1. Study areas and selection of sampling stations

We selected four rivers for study; these were the Awano River (AR) and Ayaragi River (AyR), with lengths and basin areas of 74.7 km and 185.9 km^2 and 18.6 km and 37.9 km^2, respectively, which flow into the SJ, and the Asa River (AsR) and Majime River (MR), with lengths and basin areas of 44 km and 232 km^2 and 10.2 km and 18.8 km^2 respectively, which flow into the SIS in Yamaguchi Prefecture, Japan. Each of them are small-scale rivers. Sampling stations were selected using preliminary land-use information. Sets of 100-meter by 100-meter squares area averaged land-use spatial data (herein, referred to as Japanese standard 100-m-mesh data) were obtained for these river basins from the National Land Numerical Information (NLNI) services of Japan. The 250-m-mesh population data were obtained from the e-Stat Statistics of Japan. ArcGIS v.10.6.1 (Esri, USA) was used for computation. Detailed information on river basin areas and land uses are provided in the Supplementary Information (Table S3.1).

Sampling stations across the (up-, mid-, and down-) stream reaches following the longitudinal gradient of the rivers were selected based on the land-use characteristics of the basins, focusing on point and non-point sources of pollution. The selected upstream areas (AR01 from the AR; AyR01 and AyR03 from the AyR; MR01 and MR02 from the MR; AsR01−AsR03 from the AsR) were less populous and dominated by non-point sources, specifically agricultural and forest land uses. The midstream stations (AR02 and AR03, AyR02 and AyR04, AsR04–AsR05, and MR03) were affected by both point sources, as they were moderately populated and affected by urban and residential areas and WWTPs, as well as non-point sources (agricultural and forest areas). Downstream stations (AR04–AR05, AyR05–AyR08, AsR06–AsR08, and MR04–MR08) were largely affected by both point and non-point sources due to high population densities, and domestic, agricultural, urban, and residential land uses (Fig. 3.1).

3.2.2. Sample collection

Both net-based (e.g., plankton nets, neuston nets, bongo nets, and manta trawls) and grab-based sampling methods exist for sampling surface waters. Net sampling methods tend to result in the underestimation of MPs abundances because the mesh sizes (>300 μm) that have been commonly used in numerous studies, are unable to capture environmentally ubiquitous MPs that are smaller than the mesh sizes used. Therefore, grab sampling was employed in this study due to its suitability for capturing smaller MPs particles and fibers (Li et al., 2018; Barrows et al., 2017, 2018; Green et al., 2018; Dai et al., 2018; Whitaker et al., 2019; Eo et al., 2018; Brandon et al., 2019; Watkins et al., 2019). Sampling was performed following the protocol set out in Barrows et al. (2017). In brief, we collected 1 L of river surface water samples from each of the selected stations (n = 29) from the top 5 cm surface water layer. Glass jars were used for sampling and all sampling materials and apparatuses were cleaned and prepared beforehand. Samples were collected on 09 and 10 September 2019.

3.2.3. Sample preparation and laboratory analyses

We employed membrane filtration, density separation, and wet peroxidation (WPO) methods for extraction of MPs (Gago et al., 2019; Masura et al., 2015; Barrows et al., 2017; Watkins et al., 2019; Rodrigues et al., 2018). In brief, 1 L of water sample was filtered using a 1-µm polytetrafluoroethylene (PTFE) membrane (Omnipore^{TM}, Ireland). Then, WPO was employed to remove the organic matter from the extracted particles using a 20-mL $FeSO_4 \cdot 7H_2O$ solution, 20 mL of 30% H_2O_2, and digested at 70ºC on a hotplate (Masura et al., 2015). Density separation was performed using a prepared $ZnCl_2$ solution with a density of 1.5 g/cm^3 (972 g $ZnCl_2$ per 1 L of H_2O) that was poured into a beaker (Coppock et al., 2017); particles were then allowed to settle for at least 24 hours. The supernatant was passed through stainless steel sieves (50–250, –500, –1,000, –2,000, and ~5,000 µm) and finally filtered through cellulose nitrate membrane (pore size: 5 µm; diameter: 47 mm; Omnipore^{TM}, Ireland) to extract the MP particles.

3.2.4. Microplastic identification, characterization, and data analysis

All of the extracted MP particles were visually identified, counted, and measured under a microscope (BH2, OLYMPUS, Japan) at 10x, 40x, and 100x magnification and categorized based on their shapes, sizes, and colors. ImageJ v.1.52t was used for physical measurements when the data could not be obtained directly (Schneider et al., 2012). The size-based counts were categorized into small MPs (SMPs) <1,000 µm and large MPs (LMPs) between 1,000 and 5,000 µm (Eo et al., 2018). Finally, the polymer types of each extracted particle were confirmed by Fourier transform infrared spectroscopy (FTIR) (FT/IR-4600, JASCO Corp., Ltd., Japan) equipped with an attenuated total reflection (ATR) unit. Any non-MPs particle was deducted from the counted particles. Data collection was performed using JASCO's Spectra Mananger^{TM} v.2.0 software. Background measurements were performed on a blank sample carrier prior to each sample measurement. For the measurement of each particle, 32 background scans were taken to produce spectra at a resolution of 8 cm^{-1} in infrared wavenumbers ranging from 4,000 cm^{-1} to 550 cm^{-1}. The obtained spectra were identified using the polymer spectral reference library, KnowItAll® Informatics System 2013, JASCO Edition (Bio-Rad Laboratories Inc., USA). All of the abundance-based proportions were calculated based on the number of particles. Statistical analyses were performed using Microsoft Excel 2016 v.16.0.13328.20350 (Microsoft Corp., USA).

3.2.5. Quality assurance/quality control (QA/QC)

All of the experimental equipments were rinsed thoroughly with deionized water before use. Plastic materials were avoided by replacing them with non-plastics when possible; however, when plastics were used, they were rinsed thoroughly with deionized water before use and microscopic inspection was conducted if the plastics produced MPs. However, no laboratory plastic fragments were found. Cotton laboratory coats, masks, and nitrile gloves were worn, and glassware and metalware were used. Samples were always covered with aluminum foil throughout the laboratory experiments to avoid external contamination. Reagents were prefiltered through PTFE membrane filters (pore size: 1 µm; diameter: 47 mm; Omnipore^{TM}, Ireland). Procedural blank tests and control measures were carried out during the experiment. No positive results due to indoor airborne MPs were observed during the experiment. After extraction of MPs, the samples were placed into glass Petri dishes covered with aluminum foil. The covered dishes were placed in a glass desiccator to prevent airborne contamination.

3.2.6. Microplastic loadings into the SJ and SIS Marine Environments

Loadings of MPs into the SIS and SJ by the selected rivers were calculated assuming that the MPs were distributed throughout the water columns along the river stations (Lenaker et al., 2019; Choy et al., 2019; Song et al., 2018). The available hydrographic data for our study period were collected from the River Planning Division of Yamaguchi Prefecture. No rainfall was observed during the sampling period; thus, we assumed that the river flow rates were not affected by rainfall. The MPs particle numbers and weight-based loadings were calculated utilizing the following equation:

$$L_{MPs} = Q \times 1{,}000 \times C_{i(n)} \text{ or } C_{i(wt)}, \quad (1)$$

where L_{MPs} denotes the loading of MPs, Q is the flow rate (Ls^{-1}), which was converted to (Ls^{-1}) from (m^3s^{-1}) multiplying by 1,000, $C_{i(n)}$ represents the MPs concentration by number per liter (n/L), and $C_{i(wt)}$ is the MPs concentration by weight per liter (mg/L).

The weight-based loadings of the rivers were calculated by converting the MP numbers to weights according to the shapes, sizes, and polymer densities, as weight is the result of the volume and density of the particles (Eo et al., 2019); 1.16 g/cm^3 was the measured mean polymer density in this study. The MP particle volumes were calculated following the identified shapes. The non-fiber particles (fragments and films) were flat; thus, overestimation was reduced by assuming a flat shape multiplied by 0.1, and the fibers were calculated as cylinders with a measured mean diameter of 20 µm (Eo et al., 2019; Cozar et al., 2014). The weights of non-fiber MPs particles were calculated as:

$$W_{MPs} = \frac{4}{3}\pi r^3 \times 1.16 \times \alpha, \quad (2)$$

while those of MPs fibers were given by:

$$W_{MPs} = \pi r^2 h \times 1.16, \quad (3)$$

where r is the radius of the non-fiber MPs. For MP fibers, the measured average radius (10 µm) was used. α is the shape factor (0.1 for fragments and films) and h is the measured length of each fiber.

3.2.7. Pollution load index and ecological risk assessment

The MP pollution load index (*PLI*) refers to the abundance data in the studied rivers and was calculated following the *PLI* proposed by Tomlinson et al. (1980) to assess the level of pollution in aquatic systems. The *PLI* is known as a standardized monitoring and assessment approach for determining pollution levels between different stations. Sites are considered to be polluted when $PLI > 1$ (Tomlinson et al., 1980). The *PLI* was calculated as follows:

$$PLI_i = C_i / C_o \quad (4)$$

$$PLI_{river} = \sqrt[n]{PLI_1 \times PLI_2 \times PLI_3 \cdots\cdots PLI_n}, \quad (5)$$

where i represents a station, n is the number of stations in a river, C_i is the MP abundance at station i, and C_o is the minimum baseline concentration taken from the available literature. However, due to lack of

available background data in similar environments and the analytical context of this study, the obtained lowest MP abundance among the rivers in this study was taken as the baseline concentration. Here, PLI_i is the pollution load index at station i and PLI_{river} is the riverine MPs pollution load index, which is the nth root of the total MP pollution load indices multiplied together.

We developed a pollution risk formula to assess MPs pollution risks for stations and rivers. The polymeric risks were assessed utilizing hazard scores from Lithner et al. (2011) as the chemical toxicity coefficient for the identified MPs polymers. Both the MPs abundances and chemical toxicity coefficients of the identified MPs polymers were utilized to assess MPs pollution risks. The assessments were performed using the following formulae:

$$H_i = \sum_{j=1}^{m}\{(P_{ji}/\,C_i)\ \times S_j\} \quad (6)$$

$$H_{river} = \sqrt[n]{H_1 \times H_2 \times H_3 \ldots\ldots\ldots \times H_n}\,, \quad (7)$$

where j represents a polymer type (e. g., polyethylene (PE), polypropylene (PP), polystyrene (PS), etc.), m is the number of the identified polymer types, P_{ji} is the number of each single MPs polymer identified at station i, and S_j is the risk score for each single MPs polymer taken from Lithner et al. (2011). For example, the S_j values for each of the specific single polymers were as follows: PE: 11, PP: 1, PS: 30 and so on (Table S3.2). Finally, H_i is the summation of MPs polymeric risk indices at station i and H_{river} is the polymeric risk for the rivers, which is the nth root of the total polymeric risk scores multiplied together. We calculated the MPs pollution risks as:

$$ERI_i = H_i \times PLI_i \quad (8)$$

$$ERI_{river} = \sqrt[n]{PRI_1 \times PRI_2 \times PRI_3 \ldots\ldots\ldots \times PRI_n}\,, \quad (9)$$

where ERI_i is the MP pollution ecological risk index at the station i and ERI_{river} is the MP pollution ecological risk for the river, which is the nth root of the total ecological risk scores multiplied together. The classification of ecological risk levels was derived from Hakanson, 1980 and Lithner et al. 2011 given in Table 3.3.

3.3. Results and Discussion

3.3.1. Microplastic abundances, concentrations, and distributions by land-use type

All of the sampling sites were contaminated with MPs. Total MP particle counts were 4,779 in numbers. The mean MP abundance were found 164.79±171.91 n/L in the river surface water. The MR exhibited the highest overall abundance when compared to the other rivers, following the order of MR > AR > AsR > AyR (Table 3.1). Although MP abundances and distributions varied inconsistently across the (up-, mid-, and down-)stream stations, no significant differences were observed among them using a one-way analysis of variance (ANOVA) ($p > 0.05$), indicating that all of the stations were affected by a similar level of MP pollution (Fig. 3.1 and 3.2; Table S3.3).

The weight-based MP concentrations varied from 0.05–25.85 mg/L, with mean value of 6.67±7.12 mg/L. Concentrations varied among the river stations as follows: AR — 12.14±7.45 mg/L; MR — 9.13±7.55 mg/L; AsR — 5.42±6.47 mg/L; AyR — 2.06±1.56 mg/L. However, no significant correlations ($p > 0.05$) were found between the abundances and weight-based concentrations. As the MP weights are dependent on particle volumes and densities (Eo et al., 2019), higher particle numbers might result in higher

or lower weights, while lower particle numbers might also result in higher or lower weights. For instance, the MR04 station had a higher number of particles; however, they weighed comparatively less than those collected from AR05, for which the number of MPs was far less (Fig. 3.2).

The MP abundances and distributions revealed inconsistent variations among the upstream, midstream, and downstream stations. Comparatively higher abundances were observed among the midstream and downstream river stations than in the upstream stations (Fig. 3.1; Table S3.3). Stations affected by highly populated urban areas (i.e., AR02–AR03; AyR05–AyR08; AsR02–AsR04, AsR07–AsR08; MR04–MR08) were found to have higher MP abundances than other stations. Land-use patterns showed that both point (i.e., urban and residential areas, WWTPs) and non-point (i.e., agricultural) sources affected downstream and midstream stations (AR02–AR05; AyR04–AyR08; AsR04, ASR06–AsR08; MR03–MR08), which had comparatively higher abundances than those stations affected only by non-point agricultural sources and remote forest areas dominating the upstream stations (AR01, AyR01, MR01, and AsR01) (Fig. 3.1; Table S3.3). The midstream AyR02 and AsR05–AsR06 stations were only affected by non-point agricultural sources and were found to have comparatively lower abundances of MPs than the downstream stations and similar abundances to the upstream stations. This indicated that the combination of point and non-point sources might lead to higher MPs abundances in fluvial settings than only by either point or non-point sources.

The results of statistical analyses suggested that there are no significant correlations ($p > 0.05$) among the abundances, populations, and land-use patterns over point and non-point sources (Fig. S3.1). In contrast, the less populous upstream stations dominated by non-point sources and forest areas (AR02 (102 n/L), AsR01 (116 n/L), MR01 (99 n/L), and MR02 (151 n/L)) (Fig. 3.1), were found to have considerably higher numbers of MPs than those reported from many other rivers worldwide (Table 3.1). The less populated and more forested areas (e.g., MR01 and MR02) might also be affected by other environmental processes and factors, such as non-point atmospheric MPs transport (Allen et al., 2019). Overall, these findings also suggest that non-point sources can release very high numbers of MPs alongside point sources (Baldwin et al., 2016). Thus, the land-use-based basin characteristics over both point and non-point sources could cause MPs to be released and substantially influence their abundances in freshwater systems.

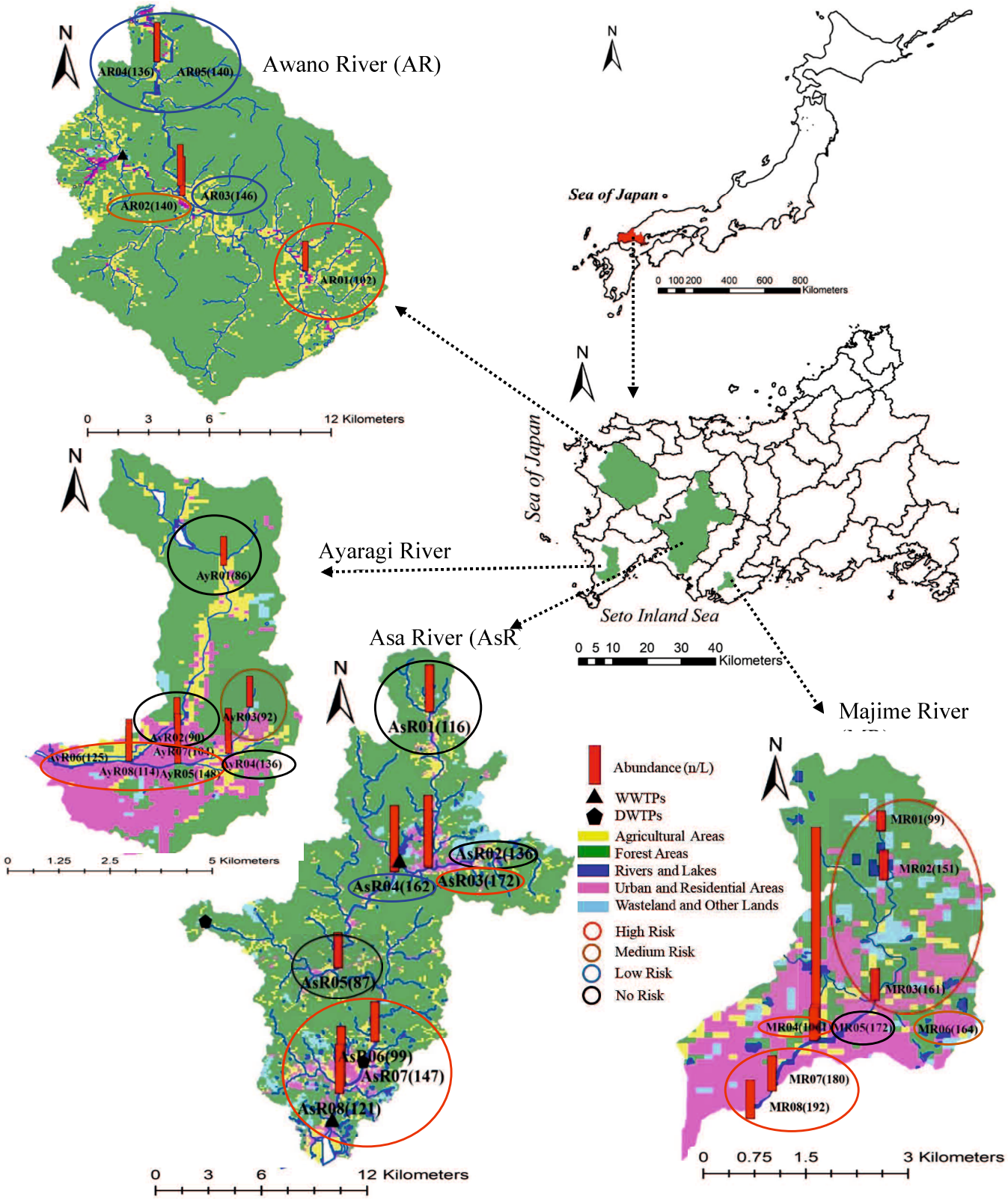


Fig. 3.1 Distributions of land uses, microplastics abundances, and risk levels among stations in the study areas of the Awano and Ayaragi rivers (Sea of Japan-flowing) and Asa and Majime rivers (Seto Inland Sea-flowing) in Yamaguchi Prefecture, Japan. Red bars represent the abundances of MPs (n/L) and circles indicate risk levels among the stations.

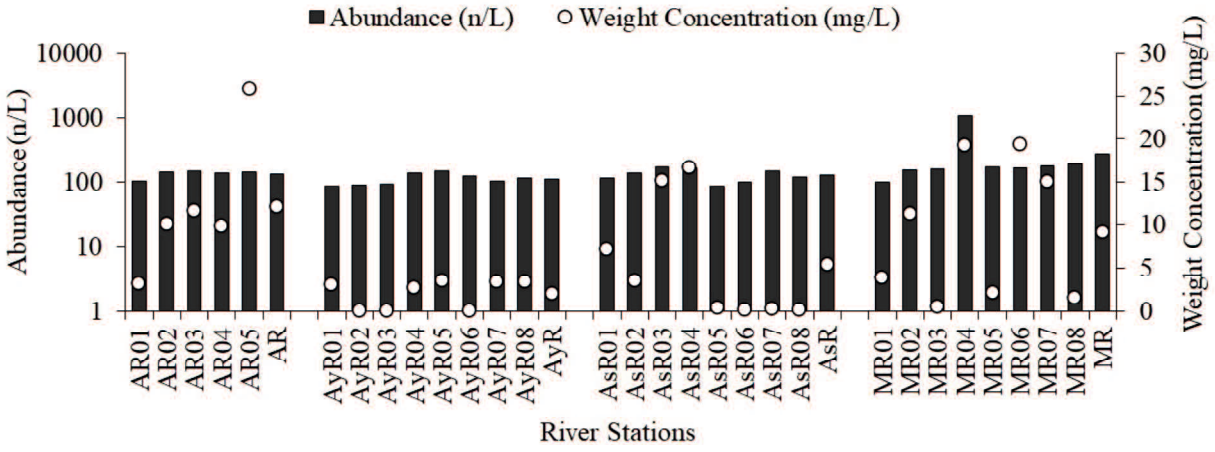


Fig. 3.2 Number-based abundances and weight concentrations of MPs and their distributions along the rivers.

3.3.2. MP pollution characteristics, occurrences, and sources

3.3.2.1. Shapes, sizes, colors, and polymer types

The shapes of the observed MPs particles were sorted into fragments, films, and fibers. Fibers (61.71%) were the predominant shape among all extracted MPs, followed by fragments (34.46%) and films (3.83%). With respect to their distributions, all of the AR stations exhibited similar proportions of these shapes. The upstream AyR stations had comparatively higher proportions of fibers than the AyR downstream stations. In the AsR, all stations exhibited similar proportions of fibers and fragments but the AsR03 station had a higher proportion of fragments. In the MR, all stations exhibited similar proportion of fibers and fragments, except for station MR04, which was found to be primarily affected by MPs fragments (Fig. 3.3).

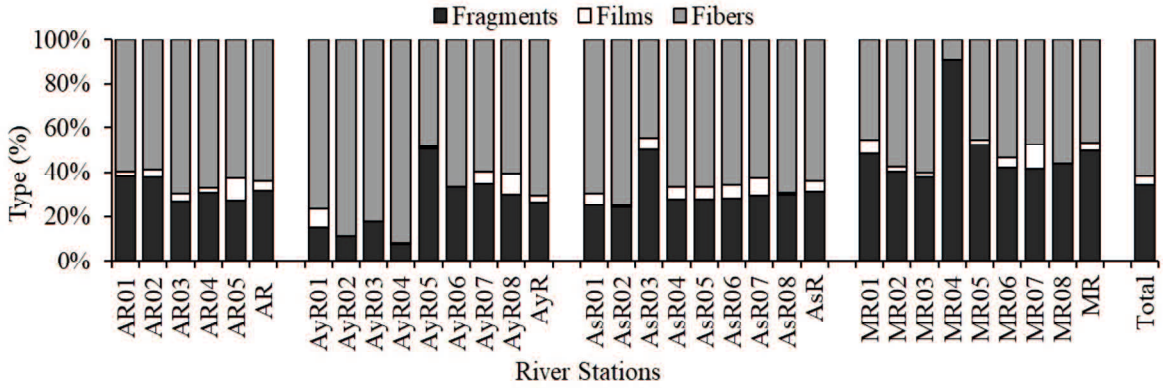


Fig. 3.3 Shape-based proportions of MPs of all the extracted particle numbers and their distributions

Each of the water samples was contaminated with different sizes of MPs. These results revealed that the SMPs (i.e., those <1,000 μm in size) accounted for the higher proportion of all identified MPs (74.65%), followed by LMPs (i.e., 1,000–5,000 μm; 25.35%). From a distribution perspective, SMPs were similarly

predominant among all stations in each river (Fig. 3.4). Additionally, characterizations based on shape–size (i.e., aspect ratio) showed that all the shapes (fragments, films, and fibers) occupied major proportions of the SMPs (Fig. S3.2). Furthermore, all of the extracted MPs particles could be sorted into visually obvious colors, among which transparent MPs were predominant (44.86%), followed by blue (28.10%), white (11.63%), green (7.47%), white (7.15%), red (5.08%), black (1.93%), and gray (0.93%). Various colorful MPs were found in the surface waters of the rivers (Fig. S3.3). Microscopic views of the extracted MPs are shown in Figure S3.4.

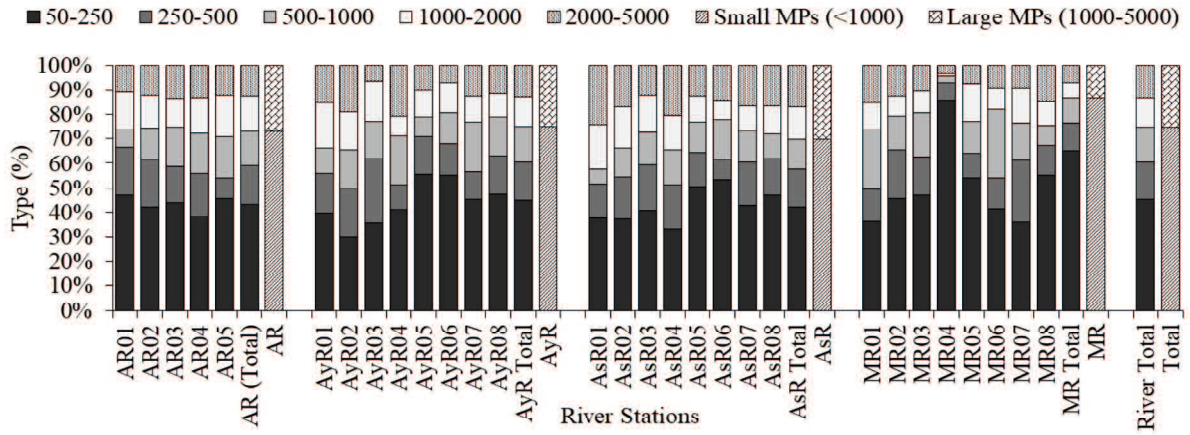


Fig. 3.4 Size-based proportions of MPs among all of the extracted particles numbers and their distributions among the river stations. All size ranges are in micrometers.

Fourteen different types of polymers were revealed via ATR-FTIR spectroscopy (Fig. 3.5). All the spectra for these polymers are shown in Fig. S3.5. The results showed that PP (27.32%), PE (20.76%), PET (13.41%), Vinylon (10.34%) (first reported polymer, similar polymer to PVA, invented in Japan in 1939 by Ichiro Sakurada [Sakurada et al., 1985]), and PS (8.04%) were the predominant polymers, followed by PAN (5.31%), PPS (4.58%), PVA (4.06%), nylon 6 (2.26%), ABS (1.49%), EPDM (1.30%), EP (0.80%), PCL (0.33%), and PBT (0.02%). With respect to their distributions, all of the predominant polymers were commonly found among all river stations. Along with the predominant polymers, the non-predominant polymers also contributed substantial proportions at several river stations (e.g., EP at AR01, Nylon 6 at AR03–AR04, EPDM at AyR05–AR06 and MR01–MR03, ABS at AsR03, PPS at MR01–MR03, and PAN at the AyR05–AyR08, AsR06–AsR08, MR01–03 and MR06–MR08 stations).

Overall, the MP polymer types and their abundance-based proportions differed among the upstream, midstream, and downstream stations. However, each of the upstream, midstream, and downstream stations of each river demonstrated similar combinations and proportions of polymer types (Fig. 3.5). These findings indicate that the associated land-use-based sources affected the occurrence of MP polymers. Thus, we speculated that the specific land-use affected the polymer types of MPs rather than their abundances. The shapes and colors of the identified polymers are given in Table S3.4.

3.3.2.2. Occurrences and sources of pollution

The identified polymers are produced for use across all aspects of modern daily life (Plastics Europe, 2019). The predominant polymers (PE, PP, PET, Vinylon, PVA, and PS) constituted 78% of the total MPs in this study. The findings of the predominant polymers were consistent with the results of previous studies worldwide (Table 3.1). Furthermore, data on the production and consumption of plastic revealed that PE, PP, PS, PET, and PVA constituted 57% of the total production in 2019 in Japan. All the identified MP polymers were representative (67%) of the total plastic production in 2019 for Japan (Japan Plastics Industry Federation (JPIF), 2019). Plastic Europe (2019) reported that PE, PP, PS, and PET constituted 65.2% of the total demand for plastics worldwide. Thus, widespread consumption was the main source of MPs pollution, both in Japan and globally.

The ubiquity of the predominant MP polymers along all river stations indicated that both point sources and non-point sources may release them due to their widespread uses and applications. All the identified MP polymers, uses and applications are given in the Table S3.2. Polyethylene, PP, PS, and PET were found as fibers, fragments, and films (Table S3.4); they are commonly known as "single-use" plastics, which are mainly originated from domestic, industrial, and commercial agricultural and urban sources. These plastics have relatively short useful lifetimes, often rapidly ending up in waste streams and litters, and thus contributing to MPs pollution (UNEP, 2018; GESAMP, 2016; Plastic Europe, 2019).

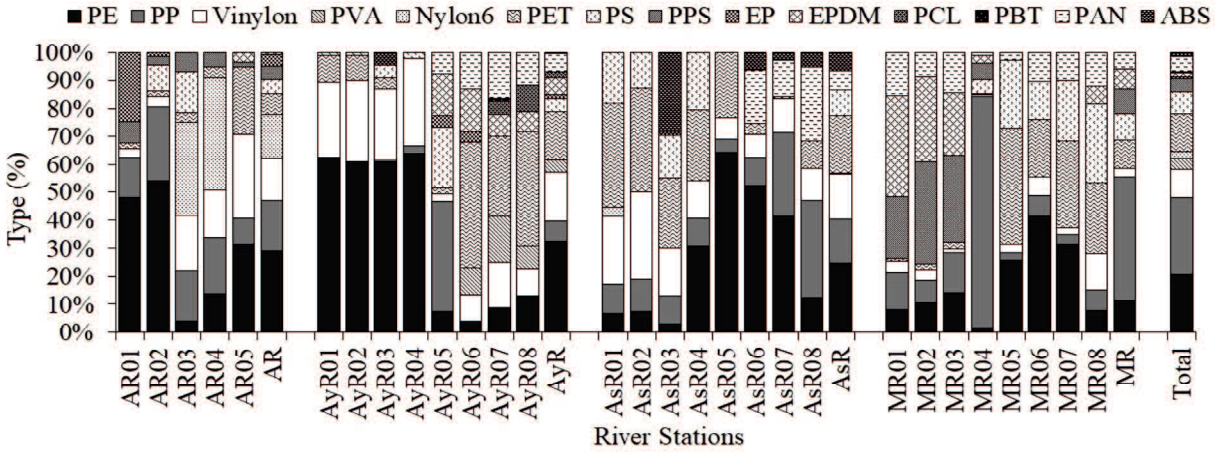


Fig. 3.5 Proportions of MPs polymers among all of the extracted particles numbers and their distributions among the river stations.

Vinylon and PET fibers have widespread application in textiles, as clothing, ropes, fishing nets, and in agriculture. These polymers are ubiquitous in the studied riverine systems. Meanwhile, polyacrylonitrile (PAN) fibers were primarily found at urban sites, with higher populations inhibiting downstream areas (e.g., AyR05–AyR08 and AsR06–AsR08), and were present everywhere among all urban and high-population-density sites in the MR. Polyphenylene sulfide (PPS) fibers were abundant in the AR and MR, mostly at remote upstream stations affected by agricultural and non-populous areas. Nylon 6 fibers were most commonly abundant in the midstream and downstream reaches of the AR, while very low amounts were observed in the AsR, which might come from ropes used by agricultural firms in these areas (Fig. 3.5). 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 might release vast

quantities of Vinylon, PET, PAN, PPS, and Nylon 6 fibers into Japanese rivers (Browne et al., 2011; Napper and Thompson, 2016; Hernandez et al., 2017; Conley et al., 2019; GESAMP, 2016; Huang et al., 2020; Henry et al., 2019; Horton and Dixon, 2018; Nizzetto et al., 2016b). Other sources of aquatic MP fibers include atmospheric fallout, deposition, and airborne transport to remote areas, which likely drive the occurrences of PPS and PAN fibers in the remote areas of the AR and MR catchments (Dris et al., 2016; Chen et al., 2019; Allen et al., 2019).

Ethylene propylene diene monomer — a durable synthetic rubber — was recorded at the urban downstream stations of the AyR (AyR05–08) and the upstream stations of the MR (MR01–MR03 and MR08), while ABS was abundant at the urban sites affecting the upstream and downstream stations of the AsR (AsR03, AsR06–AsR08) and AyR (AyR03) (Fig. 3.5). Their automotive, construction, electrical, and household applications (Table S3.2) suggest that tire wear from vehicles on roads, along with other urban land uses over residential areas, might release these synthetic rubber particles into the rivers. Moreover, urban land use has been a major contributor to tire wear-derived MP particles, which are transported into aquatic environments from roadside and stormwater runoff (Wagner et al., 2018).

Epoxy resin (EP) was found in the agricultural areas affected by upstream sites of the AR, while urban areas affected the downstream sites of the AyR, and might be sourced from agricultural firms and urban uses, including tire wear, and the products and materials used for building-construction, electronics etc. (Valášek et al., 2014; Verschoor et al., 2016; Jin et al., 2015). Very low proportions of PBTs were found in the downstream reaches of the AyR, and may be derived from recording tapes, disk films, and industrial uses (Table S3.2). Moreover, MPs are intentionally added during plastic production for households use, industrial detergents, cleaning and personal care products, paints, and agricultural fertilizers, all of which may be released into aquatic environments (Scudo et al., 2017). Overall, various land-use-based point and non-point sources may contribute to the release of MPs, affecting the polymer types found in freshwater environments.

3.3.2.3. Comparison of MP pollution

The abundances of MPs in the studied rivers were compared with those other studies worldwide in which similar analytical methods were employed. Comparisons revealed similar abundances to the Mississippi River (USA). Meanwhile, MP abundances were hundred times more abundant in the studied rivers of Japan than in the Gallatin River (USA), one hundred fifty times than Hudson River (USA), five times more abundant than in the Pearl River, ten times higher than Wei River of China, and one to four times less abundant than in in Saigon River (Vietnam). Overall, higher abundances of MPs were found in these rivers than in others globally, indicating that these small-scale freshwater systems are more vulnerable to MP pollution. Furthermore, fibers, films, fragments, SMPs, and PE, PP, and PET have been commonly reported in the surface waters of rivers worldwide, as well as in this study (Table 3.1). Notably, the grab sampling employed here may have led to the recording of higher MP abundances because of the quantification of smaller particles (<300 μm), which were extremely abundant (Fig. 3.4) (Barrows et al., 2017; Green et al., 2018).

Table 3.1 Summary of microplastic abundances in various riverine environments worldwide.

Study Area	Length (km)	Basin Area (km^2)	Abundance (n/L)	Major Characteristics			References
			Min. – Max. (Mean±SD)	Size (µm)	Shape	Polymer	
Awano River, Japan	29.3	177	102–146 (132.80±15.73)	50–1,000	Fibers	PE, PP, Vinylon	This study
Ayaragi River, Japan	9.5	20	86–148 (111.88±21.42)	50–1,000	Fibers	PE, Vinylon, PET	This study
Asa River, Japan	44	232	87–172 (130±27.84)	50–1,000	Fibers	PE, PP, Vinylon	This study
Majime River, Japan	8.3	12	99–1061 (272.5±299.15)	50–1,000	Fibers, Fragments	PP, PET, PP, PS	This study
Gallatin River, USA	193	28,490	0–67.5 (1.2)	100–1,500	Fibers	PET	Barrows et al., 2018
Mississippi River, USA	3778	2,980,000	0–172	30–90	Fragments	PET, PE, PP	Scircle et al., 2020
Hudson River, USA	507	36,260	0.38–12.38 (0.98)	330–3,590	Fibers	PET, Teflon, PP	Miller et al., 2017
Saigon River, Vietnam	250	4,771	172–519	50–250	Fibers, Fragments	PET, PE, PP	Lahens et al., 2018
Pearl River, China	2400	453,700	8.7–53	50–500	Films, Fibers	PA, Cellophane	Yan et al., 2019
Wei River, China	818	135,000	3.67–10.7	75–500	Film, Fragments	PE, PS	Ding et al., 2019
Nakdong River, South Korea	510	23,380	0.29–4.76	20–300	Fiber, Fragments	PP, PET	Eo et al., 2019
Yellow River, China	5464	752,443	380–1392	50–200	Fibers	PE, PP, PS	Han et al., 2020
Antua River, Portugal	38	149	0.06–1.26	--	Foams, Fibers	PE, PP	Rodrigues et al., 2018
Snake and Lower Columbia Rivers, USA	1735	240,765	0–5.40 (0.91 ± 1.14)	100–333	Fibers, Films,	PP, PE, PET	Kapp and Yeatman, 2018
Tibet Plateau Rivers, China			0.48–0.967	< 1,000	Fibers	PET, PE, PP	Jiang et al., 2019

3.3.3. Loads of MPs transported to the SIS and SJ by the rivers

The estimated loadings per day into the SIS and SJ by the four Japanese rivers are given in Table 3.2. The Asa River (AsR) was the highest MPs loading river by numbers (154.27 billion/day) and discharged into the SIS. The Awano River (AR) was the second highest by numbers (95.7 billion/day) but top by weight-based (17.55 billion/day) MPs loading and released into SJ. The Ayaragi (AyR) and Majime (MR) rivers loaded lower amounts of MPs in the SIS and SJ than the AR and AsR. In comparison to the larger Nakdong River in South Korea (Eo et al., 2019), the AR and AsR rivers displayed substantially higher (six to eleven times by numbers and one to hundred times by weight) MP loadings into the marine environments. Miller et al. (2017) estimated that ~300 million microfibers are transported into the Atlantic Ocean by the Hudson River (USA) and Scircle et al. (2020) estimated that 129 trillion MPs are transported by the Mississippi River (USA) (Table 3.2). These values were considerably higher than our estimates. However, the river types, drainage basin areas, and land-use-based sources, are comparable to MP loadings (Schimdt et al., 2017). Our studied rivers had significantly smaller basin areas than the compared rivers (Table 3.2). Therefore, we also compared their loadings per basin area. In this context, when compared to the Nakdong, Hudson, and Mississippi rivers, we found higher loading of MPs per basin area by the small-scale Japanese rivers, suggesting that these small-scale basins are vital sources of MPs to affect their respective fluvial systems, as well as the SJ and SIS marine environments. Overall, the studied Japanese rivers emitted substantially higher amounts of land-sourced MPs into their receiving marine environments as per basin area (Table 3.2).

MP loadings varied substantially under different hydrological regimes, represented in this study by flow rates. Although the MR had higher abundances of MPs than the AsR and AR, its loadings into the receiving marine environments were lower due to its discharge rate (Table 3.2). Riverine MP export is affected by other hydrological and meteorological conditions, such as water column transport, seasonal variations, weather, rainfall, and climatic events, as well as the generation of mismanaged plastic wastes in river catchments and land-use characteristics within the basin (Schimdt et al., 2017; Lebreton et al., 2017; Kataoka et al., 2018; Xia et al., 2020; van Emmerik et al., 2018). Thus, it is possible to overestimate or underestimate riverine MP loadings, irrespective of these regulating factors, and consideration of these factors are recommended to yield more realistic estimates and empirical analyses of the annual loads of MPs to marine environments (Eo et al., 2019; Schimdt et al., 2017).

To verify the influences of land-sourced MPs on the SIS and SJ, we compared the MP types between the studied rivers and the SJ and SIS from our previous study (Kabir et al., 2020a). The identification of the same predominant polymer types (PE, PP, PVA, PET, and PS), shapes (fibers and fragments), and sizes (SMPs) in these rivers and the receiving SJ and SIS indicated that Japan land-sourced MPs might have largely influenced the MP pollution in SJ and SIS marine environments, in addition to the foreign areas originated plastics and MP pollution in the SJ (Kabir et al., 2020a). The finding of substantial amounts of MPs emission into receiving marine environments indicated that large amounts of MPs are being generated on land and reaching to marine environments along with the subsequent macro-plastics degradation into MPs secondarily in the ocean. This suggested to control MPs at sources. Prominently, the studied rivers are key conduits for exporting these land-sourced MPs into the sinks of the SIS and SJ. However, fluvial sediments also retain MPs and bioavailability might occur in these systems, hence, recommended for further comprehensive investigations in order to understand the fate of MPs and pollution in riverine environments (Nizzetto et al., 2016a; de Sa et al., 2018).

Table 3.2 Microplastic loadings in the studied rivers and their receiving environments.

Rivers	Basin Area (km^2)	Avg. Flow Rate (L/s)	Loadings		Loadings by Basin Areas		Receiving Environments	References
			Number (billion/day)	Weight (ton/day)	Number (billion/day/km^2)	Weight (ton/day/km^2)		
Awano River (AR)	177* (185.9)	7,860	95.7	17.55	0.54	0.1	Sea of Japan (SJ)	This Study
Ayaragi River (AyR)	20* (37.9)	40	0.4	0.01	0.02	0.0005	Sea of Japan (SJ)	This Study
Asa River (AsR)	232* (232)	14,756.5	154.27	0.14	63.6	0.0006	Seto Inland Sea (SIS)	This Study
Majime River (MR)	12* (18.8)	210	3.48	0.03	0.29	0.0025	Seto Inland Sea (SIS)	This Study
Nakdong River	6261* (21,588)	150,500	14.8	0.15	0.002	0.00002	South Sea (Korea Strait)	Eo et al., 2019
Hudson River, USA	21,565* (33,000)	104,789	300		0.014		Atlantic Ocean	Miller et al., 2017
Mississippi River	1,310,137* (3,224,535)	29,025,000	129,000		0.1		New Orleans, Mississippi River	Scircle et al., 2020**

*The covered basin areas of total basin areas in those studies.

** The covered basin areas were obtained by personal communication by email with the corresponding author.

3.3.4. Microplastic pollution load index, ecological risk assessment, and pollution hotspots

The *PLI* results clearly indicated that all stations and rivers were polluted with MPs ($PLI > 1$) and suggested similar levels of pollution at all stations except MR04, which had a higher abundance of MPs, found higher pollution level than the other sites by means of PLI_i (Fig. 3.6, Table 3.3). As the *PLI* mainly refers to the abundance of MPs, the increased abundance of MPs resulted in a higher pollution load. Assessments of polymeric risks (*H*) and ecological risks (*ERI*) are also needed to develop a clear understanding of the pollution risks relative to *PLI*-based pollution levels.

When considering the H_i values, they were found to differ among the stations in all rivers. The results showed that polymeric risks varied from low to high. The AR01 Ay05–Ay08, AsR03, AsR06–AsR08, and MR01–03 and MR06–08 stations were found to be at high risks for MPs polymers (Fig. 3.1 and 3.6). These polymeric risks demonstrated that the presence of more toxic polymers result in higher hazard scores (ABS: 6552; PAN: 12379; EP: 7139; PPS: 897; Nylon 6: 50; PS: 30) and were high-risk indicators along the river

stations. The most toxic polymers were found to be abundant at high-risk stations polymers (Fig. 3.5 and 3.6). Although all of the highly toxic polymers that were identified were present in lower proportions than the other polymers, they still posed high risks due to their higher polymeric hazard scores, while the higher proportions of polymers with fairly low hazard scores resulted in lower polymeric risk values (Table S3.2). For example, MR04 was found to have the highest MPs abundance (Fig. 3.1 and 3.2) but posed medium polymeric risks by means of the H_i value because PP accounted for 82.66% of the total MPs load at the MR04 station (Fig. 3.5), resulting in medium polymeric risk due to the lower hazard score 1 of PP. Hence, we did not conclude that the stations with the greatest MPs abundances resulted in lower pollution risks; rather, the polymeric risk assessments were comparable with the ecological risk index (*ERI)* results. Notably, the polymeric risk assessments *H* provided insights into the presence of toxic polymers in the river environments.

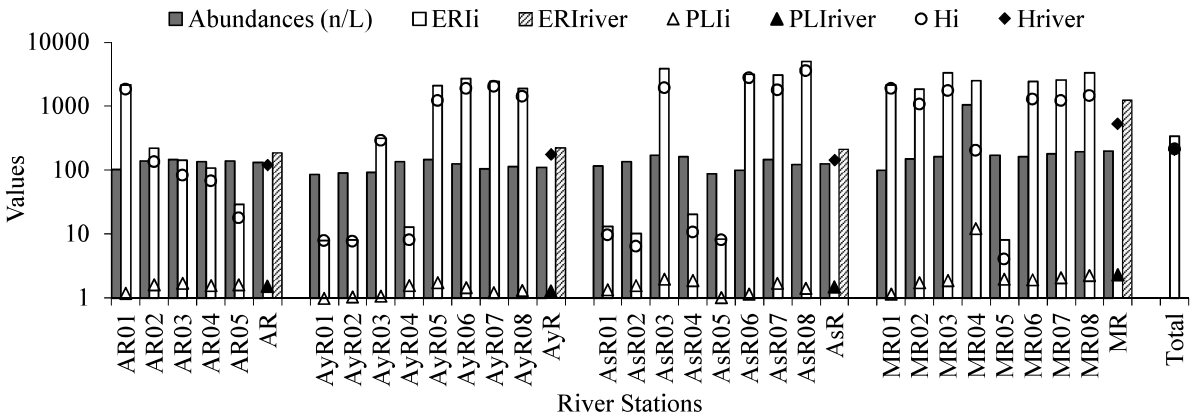


Fig. 3.6 Microplastics abundances, pollution load index (*PLI*), polymeric risk score (*H*), ecological risk index (*ERI*), and their distributions among the river stations.

The ERI_i values revealed low to very high risks among the river stations (Fig. 3.6; Table 3.3). All the lower polymeric risks H_i value demonstrating stations did not show the low ecological risks ERI_i value consistently (Fig. 3.6). For instance, the MR04, which had the highest abundance of MPs, posed a medium polymeric risk by means of H_i value but a very high risk according to the ERI_i. Hence, for the MR04, the higher MPs abundances reflected very high ecological risks. On the other hand, all of the stations posing high polymeric risks also posed high ecological risks consistently. A significant correlation ($R^2 = 0.84$) was observed between the values of *H* and *ERI* (Fig. S3.6). However, no significant correlation ($R^2 = 0.02$) was found between MPs abundance and *H* (Fig. S3.7), or between MPs abundance and *ERI* ($R^2 = 0.03$) (Fig. S3.8), indicating that not all of the similar level of MPs abundance based stations posed similarly high polymeric and pollution risks. Therefore, increased MPs pollution risks and levels were broadly dependent on the presence of toxic MP polymers, as well as the high MP abundance-based pollution loads. To state, the higher the abundances of MPs and toxic polymers were at a station, the higher were its pollution levels and risks when considering the abundances-based pollution level alone.

Considering land-uses, we found that the agricultural land-use dominating the upstream AR01 station posed high risks. All other midstream and downstream stations (AR02–AR05) were found to pose no to moderate risks. For the AyR, the agricultural, urban, and residential land-uses dominating the

downstream stations (AyR03–AyR08) exhibited high risk levels, except for AyR04, which posed a low risk, while the upstream stations (AyR01–02) were found to be at low risk. Similarly, for the AsR, all of the downstream stations (AsR06–08), which were affected by agricultural, urban, and residential land uses, exhibited high risks except for the midstream station, AsR05; meanwhile, the upstream stations (AsR01–04) exhibited low risks except for where urban and residential land-uses resulted in a high risk at station AsR03. All MR stations were found to pose similarly moderate to high risks, except for MR05. The urban, agricultural, and residential land-use-dominated MR was regarded as a very high-risk river (Fig. 3.6). Furthermore, as polymers are source-specific and land-use sources might affect the occurrences of polymers, the results of this study indicated that both point and non-point sources related to various land-uses can pose high pollution risks (Fig. 3.1) by releasing different types of polymers, including the highly toxic polymers.

Table 3.3 Categories employed in the microplastic pollution loading index (PLI), polymeric risk assessment (H), and pollution ecological risk index (ERI).

ERI	***H***	**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

Our findings suggested that abundance-based higher pollution level (i.e., *PLI*) and highly toxic polymers yield high pollution risks. Based on this result, we identified pollution hotspots those stations posed high MPs pollution ecological risks (ERI). The spatial distribution of risk zones classifications is shown in Fig. 3.1. The pollution hotspots included the following stations: AR01, AyR05–AyR06, AsR03, AsR06–AsR08, and MR01–MR03 and MR05–MR08 (Fig. 3.1). Risk-zones classification and hotspots identification may facilitate further pollution monitoring and management in this environmental context.

3.3.5. Pollution characteristics, risk exposure, and potential threats

The characteristics of MPs are influential factors for understanding pollution threats in aquatic ecosystems. We observed the dominance of SMPs (<1000 μm), fibers and fragments, the varieties of colors and diverse polymers of MPs in four small-scale Japanese rivers. Previous studies have indicated that SMPs particles cause greater hazards (Lei et al., 2018), creates higher probability of ingestion and biological transportation by aquatic organisms (Katija et al., 2017; Zheng et al., 2020). Fibers and fragments are the most commonly reported shapes of MPs in aquatic organisms (de Sa et al., 2018). MP fibers have been reported to be more toxic to aquatic biota (Ziajahromi et al., 2017). Laboratory studies have showed that MP polymers posed numerous ecotoxicological effects on aquatic organisms including mortality, reductions in growth, productivity, population sizes, and gene expression, as well as increased oxidative stress (de Sa et al., 2018). MPs ingestion and uptake can cause physical damages, such as intestinal blockages and internal abrasions (Wright et al., 2013). Moreover, the identified highly toxic polymers (ABS, PPS, PAN, EP, and PS) in this study are mutagenic, carcinogenic, and endocrine disrupting in both humans and aquatic organisms (Lithner et al., 2011; Gallo et al., 2018).

Concerns are growing regarding unavoidable exposure of MPs to human (Revel et al., 2018; Rist et al., 2018; Wright and Kelly, 2017; Cox et al., 2019; Oliveira et al., 2019). In the context of riverine ecosystems, human exposure has been linked to MPs through various pathways, including drinking water supplies, fisheries, agriculture and freshwater food commodities, and seafood consumption. For instance, drinking water treatment plants (DWTPs), with a capacity of 1580 m^3/day, exist in the AsR basin and serve a large population (i.e., 26,320 people) (Fig. 3.1). Although the DWTPs remove a great proportion of MPs during the purification processes, they still release many MPs (Novotna et al., 2019), thus posing potential risks to human health. Moreover, the bioaccumulation of MPs might also impact humans via transference through the trophic hierarchies of freshwater and marine ecosystems (Oliveira et al., 2019; Carbery et al., 2018; Nelms et al., 2018; Farrell and Nelson, 2013). Overall, in this study, the identified MP characteristics, assessed pollution risks, and potential exposures indicated numerous potential ecotoxicological threats to these riverine ecosystems, may also pose risks to inhabiting humans, as well as the ecosystems of the receiving SIS and SJ.

MPs comprise a diverse suite of toxic pollutants, acts as vectors for other organic and inorganic toxic chemical pollutants (Rochman et al., 2019), which may enhance the MPs pollution risks. Therefore, comprehensive risks assessment models need to be developed to explain MP pollution ecological risks in relation to the other toxic pollutants (Li et al., 2020). Further assessments and quantifications of MPs exposure to aquatic organisms and humans through various pathways of freshwater and marine ecosystems, as well as related ecotoxicological studies, are essential to determine the cumulative impacts of MP pollution on aquatic environments, food webs, and human health.

3.4. Conclusions

Overall, high abundances and MP pollution levels were revealed in four small-scale Japanese rivers. The SMPs in sizes, fibers and fragments in shapes were predominant. Variety of colors and polymer types were found. These rivers were found to be prominent conduits responsible for emitting very high amounts of land-sourced MPs into the SIS and SJ, thus influencing marine MPs pollution. The assessment of pollution risks showed low to high pollution risks. High pollution risks were dependent on higher MPs abundances and the presence of highly toxic polymers (ABS, PPS, PS, Nylon 6, PAN, and EP) in this study. Both point and non-point sources based on land-use could release MPs, affect the occurrences of different polymer types and posing high pollution risks. The identified MP characteristics and estimated pollution risks posed ecotoxicological threats to these freshwater ecosystems, inhabiting human populations, and the receiving SIS and SJ.

The spatial distributions of risk zones highlighted the pollution hotspots and may be used to facilitate pollution monitoring and the setting of priority management zones. The assessment of pollution risks provided insights into pollution, as well as a baseline for future comprehensive risk assessments for environmental and human health. The results of this study also suggest that small-scale rivers are crucial in the context of MP pollution and emphasize the need for prioritizing future small-scale river pollution monitoring. The knowledge gained through this study will be useful for making policies regarding water quality criteria and for strengthening our understanding of pollution for the development of upstream-to-downstream intervention strategies, pollution control and risk reduction strategies, and management approaches. Future studies towards the rigorous assessment of land-use-based pollution sources and the catchment generated mismanaged plastics and MPs are recommended.

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Supplementary Material

Table S3.1 River basin and land-use information of the studied rivers

	Area (km^2)	**Population (Density/km^2)**	**Urban**	**Agriculture**	**WWTPs**	**Forest**	**Others***
Awano River (AR)	177.02	26.71	1.51 (0.85%)	23.32 (13.17%)	1	149.88 (84.67%)	2.31 (1.31%)
Ayaragi River (AyR)	19.78	657.23	0.97 (4.89%)	2.18 (11.04%)	—	15.69 (79.35%)	0.93 (4.71%)
Asa River (AsR)	231.81	115.75	10.68 (4.61%)	27.11 (11.69%)	2	179.22 (77.31%)	14.80 (6.38%)
Majime River (MR)	12.34	1121.15	3.31 (26.83%)	0.75 (6.11%)	—	6.66 (53.95%)	1.62 (13.11%)

*Others including- athletic field, an airport, a racetrack, a baseball field, a school harbor area, an open space in an artificial land, etc.

Table S3.2 Identified microplastics polymers, their monomers, density, uses and applications, and risk scores

Polymers	Abbreviations	Monomer	Density	Applications	Observed Shapes	Risk Score (S_n)*
Polyethylene	PE	Ethylene	0.91–0.96	Reusable bags, trays and containers, agricultural firm, food packaging film, toys, milk bottles, shampoo bottles, pipes, houseware (Plastics Europe, 2019)	Fragments, Films, Fibers	11
Polypropylene	PP	Propylene	0.85–0.94	Food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, bank notes, etc. (Plastics Europe, 2019)	Fragments, Films, Fibers	1
Nylon 6		ε-caprolactam	1.14–1.15	Textiles, packaging, engineering, medical, and agriculture for having UV absorption capacity (Hu and Yang, 2000)	Fibers	50
Vinylon		Vinyl acetate	1.19	Japanese Traditional Dresses, Working Wear, Fishing Nets, seaweed farming nets, Ropes, Filter Cloth, Canvas, Sheets, Cement Reinforcement Material, Hoses, Belts, Tire Cords, Kanreisha (Open Thin Fabric), Threads for Tatami Mats, Construction Nets, Paper Making Felts, etc. (JCFA)	Fibers	1
Polyethylene Terephthalate	PET	Ethylene Glycol	1.38	Bottles for water, soft drinks, juices, cleaners (Plastic Europe, 2019)	Fibers, Fragments	4
Polystyrene	PS	Styrene	0.96–1.05	Food packaging (dairy, fishery), building insulation, electrical & electronic equipment, inner liner for fridges, eyeglasses frames, etc (Plastic Europe, 2019)	Fragments	30
Polyphenylene Sulfide	PPS	1,4-dichloro benzene	1.35	Synthetic fiber and textiles, coal boilers, papermaking felts, electrical insulation, film capacitors, specialty membranes, gaskets, and packings (Yan, 2016)	Fibers	897
Epoxy Resin	EP	Glycidyl-based epoxy resins	0.9–1.1	Manufacture of adhesives, plastics, paints, coatings, primers and sealers, flooring and other products and materials for building and construction, electronic materials (Verschoor et al., 2016; Jin et al., 2015)	Fragments, Films	7139

Table S3.2 Identified microplastics polymers, their monomers, density, uses and applications, and risk scores (Continued)

Polymers	Abbreviations	Monomer	Density	Applications	Observed Shapes	Risk Score (S_n)*
Polyacrylonitrile	PAN	Acrylonitrile	1.184	Hot gas filtration systems, outdoor awnings, sails for yachts, and fiber reinforced concrete. Fiber copolymers to make knitted clothing, like socks and sweaters, tents textiles, ultra-filtration membranes, hollow fibers for reverse osmosis, etc. Wrapping materials for foods such as tea, coffee, rice, fish, and eggs, and chemicals, drugs, electronics, and cosmetics (Sada et al., 2014).	Fibers	12379
Polybutylene terephthalate	PBT	Dimethyl terephthalate	1.30	Packaging, automotive, electrical, and consumer markets, optical fibers (Plastics Europe, 2019).	Films	N C
Polycaprolactone	PCL	ε-caprolactone	1.145	Scaffolds in tissue engineering, microparticles for drug delivery, making trash bags, microelectronics, adhesives, and packaging (Labet and Thielemans, 2009).	Films	N C
Polyvinyl Alcohol	PVA	vinyl acetate	1.19	Industries, such as textile, paper industry, and food packaging industry (Satoh, 2014).	Fragments	1
Acrylonitrile Butadiene Styrene	ABS	Styrene	1.02–1.08	Automotive applications, pipes, toys, electrical, households, 3D printing etc. (Begum et al., 2020; McKeen, 2018)	Fragments	6552

* The risk scores are taken from Lithner et al., 2011.

Table S3.3 Microplastics abundances and their potential land-use sources along upstream, midstream, and downstream stations of the studied rivers

Rivers/Stations	Abundances (n/L) (Mean SD)	Potential Land-Use Sources of MPs
Awano River (AR)	132.8±15.72	
AR01	102±0	Agricultural
AR02–AR03	143±3	Agricultural, Urban and Residential, WWTPs
AR04–AR05	138±2	Agricultural
Ayaragi River (AyR)	111.88±21.42	
AyR01, AyR03	89±3	Agricultural
AyR02, AyR04	113±23	Agricultural, Urban and Residential
AyR05–AR08	122.75±16.36	Agricultural, Urban and Residential
Asa River (AsR)	130±27.84	
AsR01–AsR03	141.33±23.17	Agricultural, Urban and Residential
AsR04–AsR05	124.5±37.5	Agricultural, WWTPs
AsR06–AR08	122.33±19.62	Agricultural, Urban and Residential
Majime River (MR)	272.5±299.15	
MR01–MR02	125±26	Residentials
MR03	161±0	Agricultural, Urban and Residential
MR04–MR08	397.25±383.36	Agricultural, Urban and Residential

N. B. : △, □, and ▽ represents for upstream, midsteam, and downstream stations respectively

Table S3.4 Identified MPs Polymers based on the shape-color characteristics

	Transparent	White	Blue	Green	Red	Grey	Black
Fragment	EP, PS, PE, PVA, EPDM	PP, PE, PS, EPDM	PP, PE	PE, PP	PET	PET, EP, EPDM	ABS, EPDM
Film	PE, PP, PCL	PBT, PE, PP	PP, PE	--	--	EP, PP	EPDM
Fiber	PE, Nylon 6, PET, PP, PPS	PPS, Vinylon, Nylon 6, PP, PE	PE, Vinylon, PAN	PP, PE, Vinylon	Vinylon, PET	Vinylon	

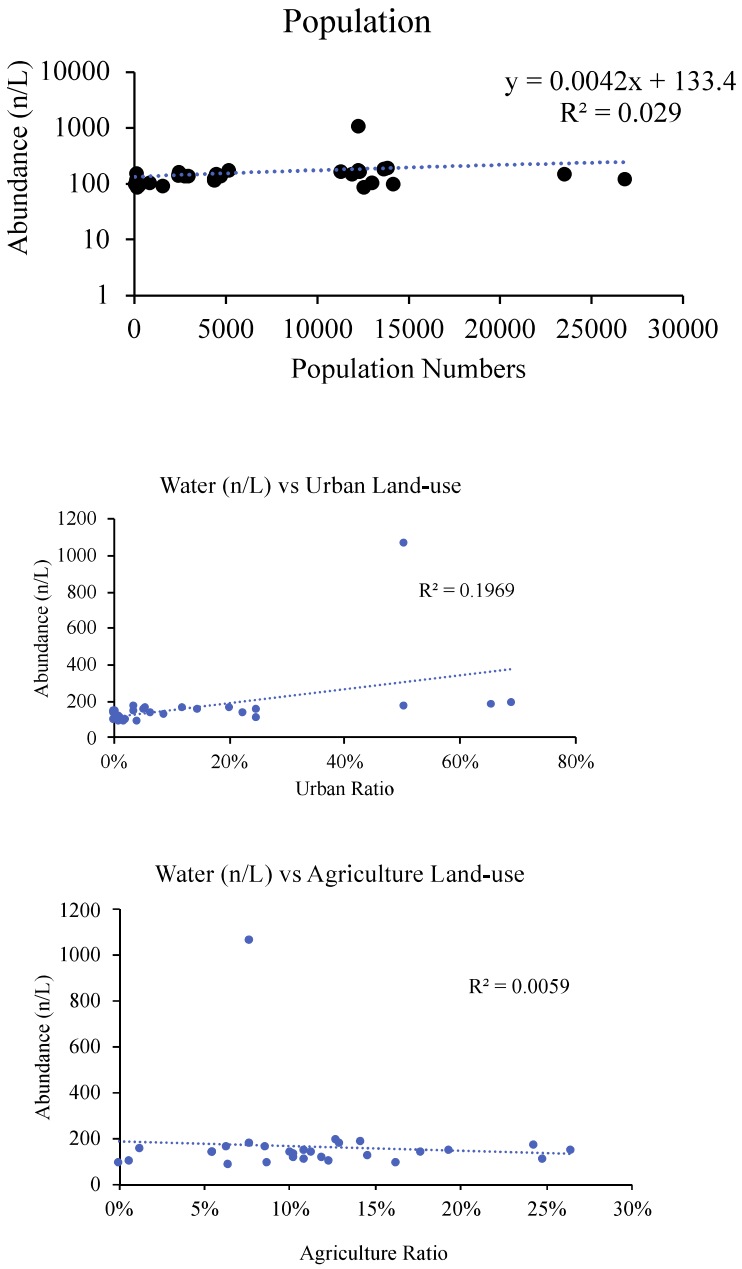


Fig. S3.1 Strength of relationship among MPs abundances and land-use patterns along the studied river basins

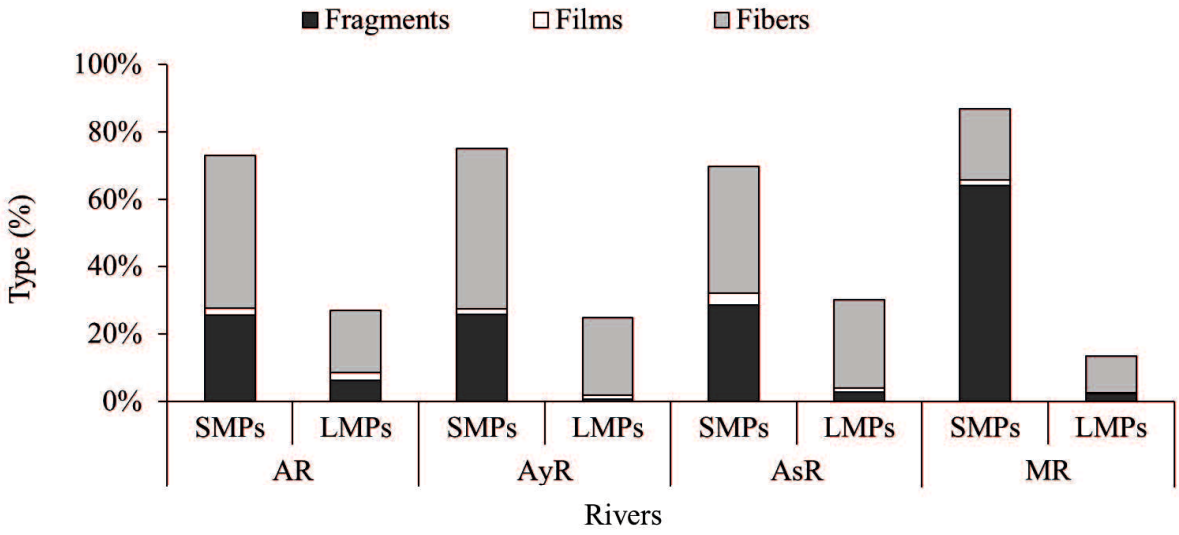


Fig. S3.2 Shape-size based microplastics proportions of the totally extracted particles numbers and their distributions along the rivers

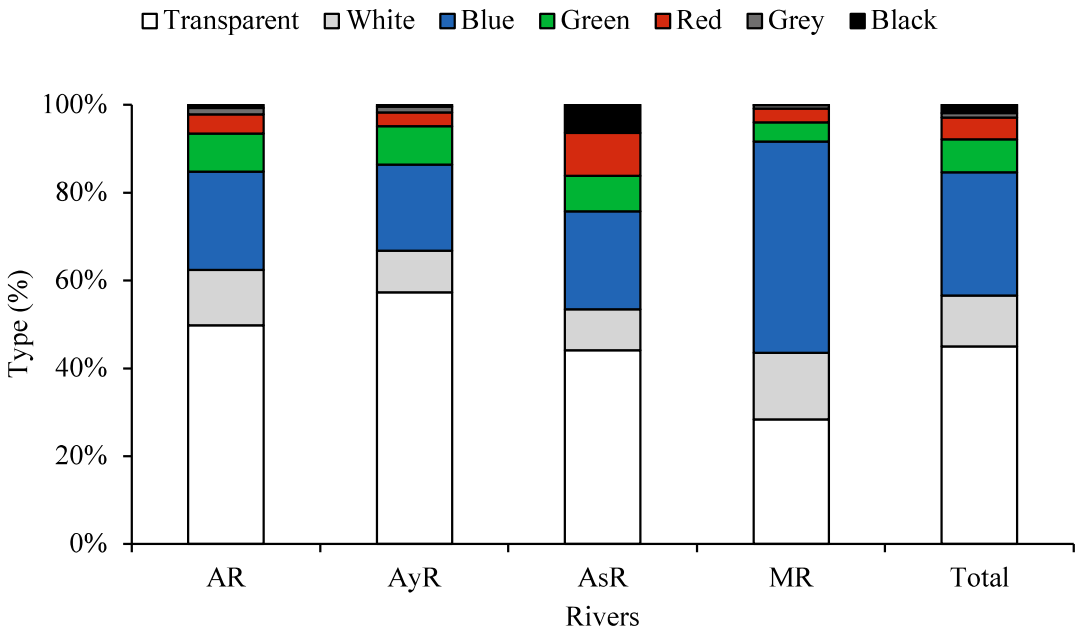


Fig. S3.3 Color based MPs distributions along the rivers

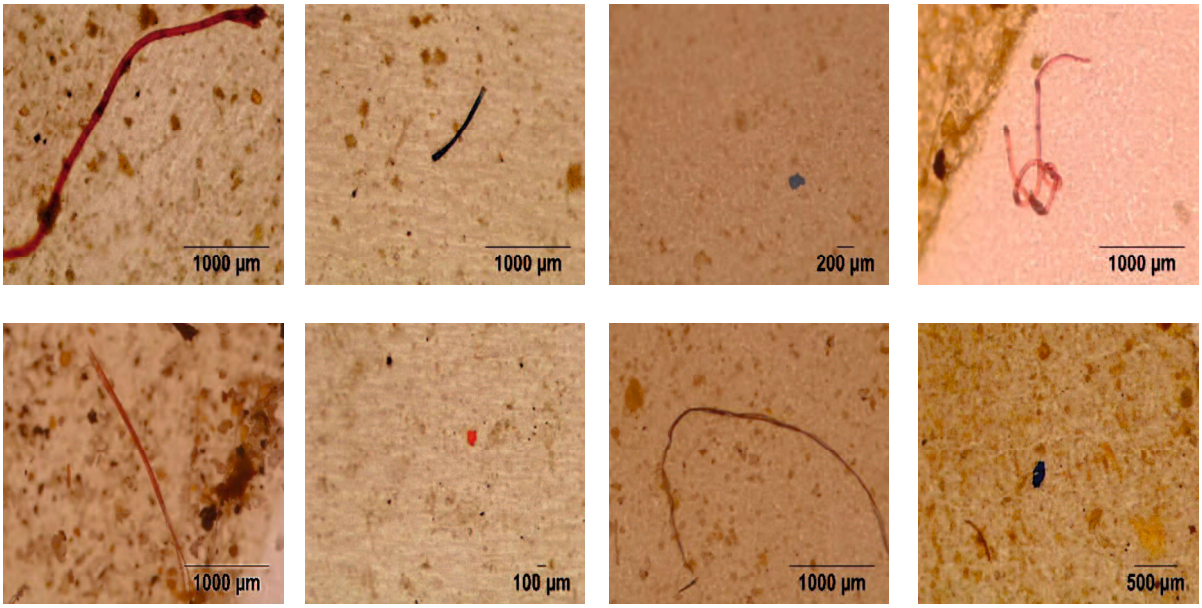
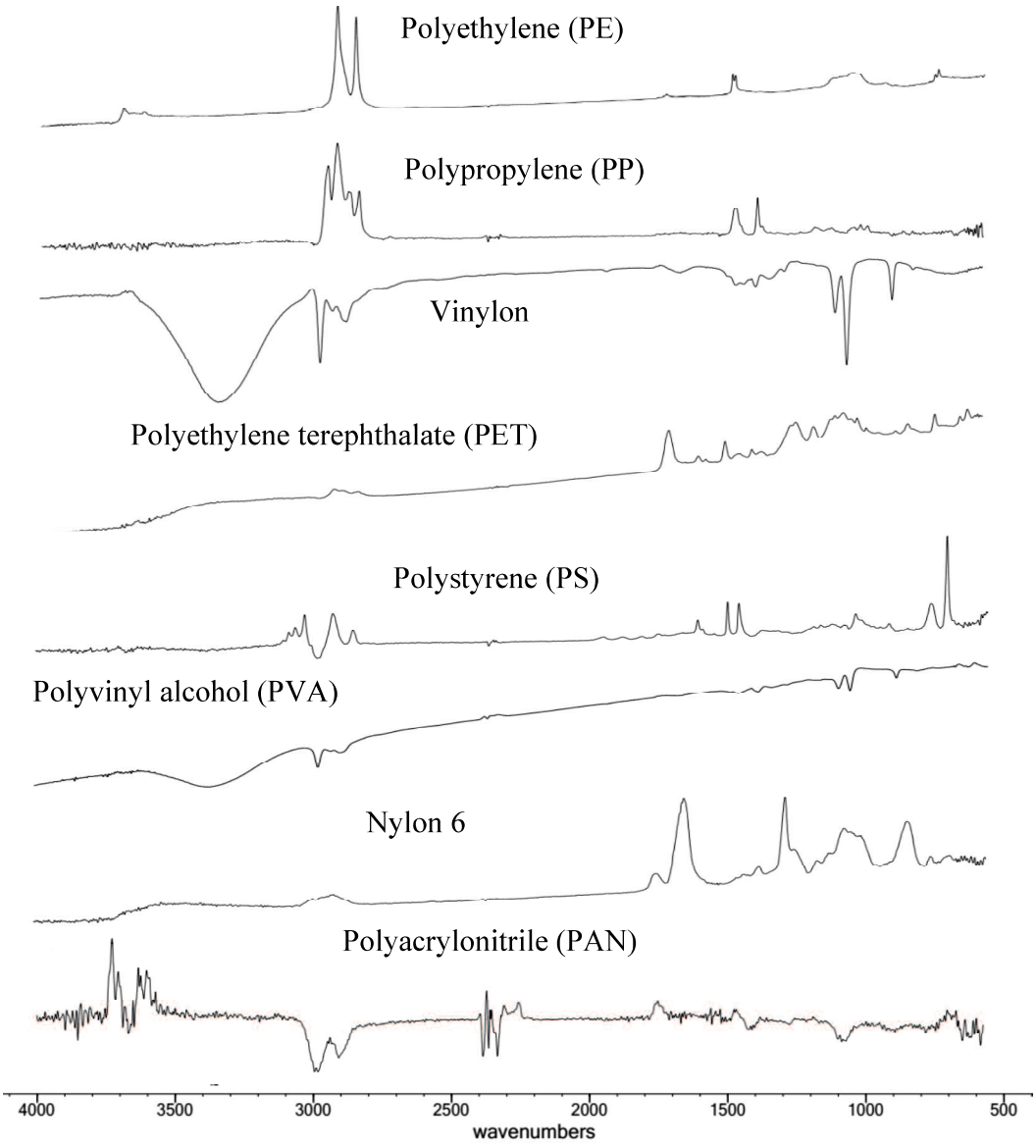


Fig. S3.4 Microscopic view of different types of microplastics extracted from the river surface water


Polyethylene (PE)
Polypropylene (PP)
Vinylon
Polyethylene terephthalate (PET)
Polystyrene (PS)
Polyvinyl alcohol (PVA)
Nylon 6
Polyacrylonitrile (PAN)
4000
3500
3000
2500
2000
1500
1000
500
wavenumbers

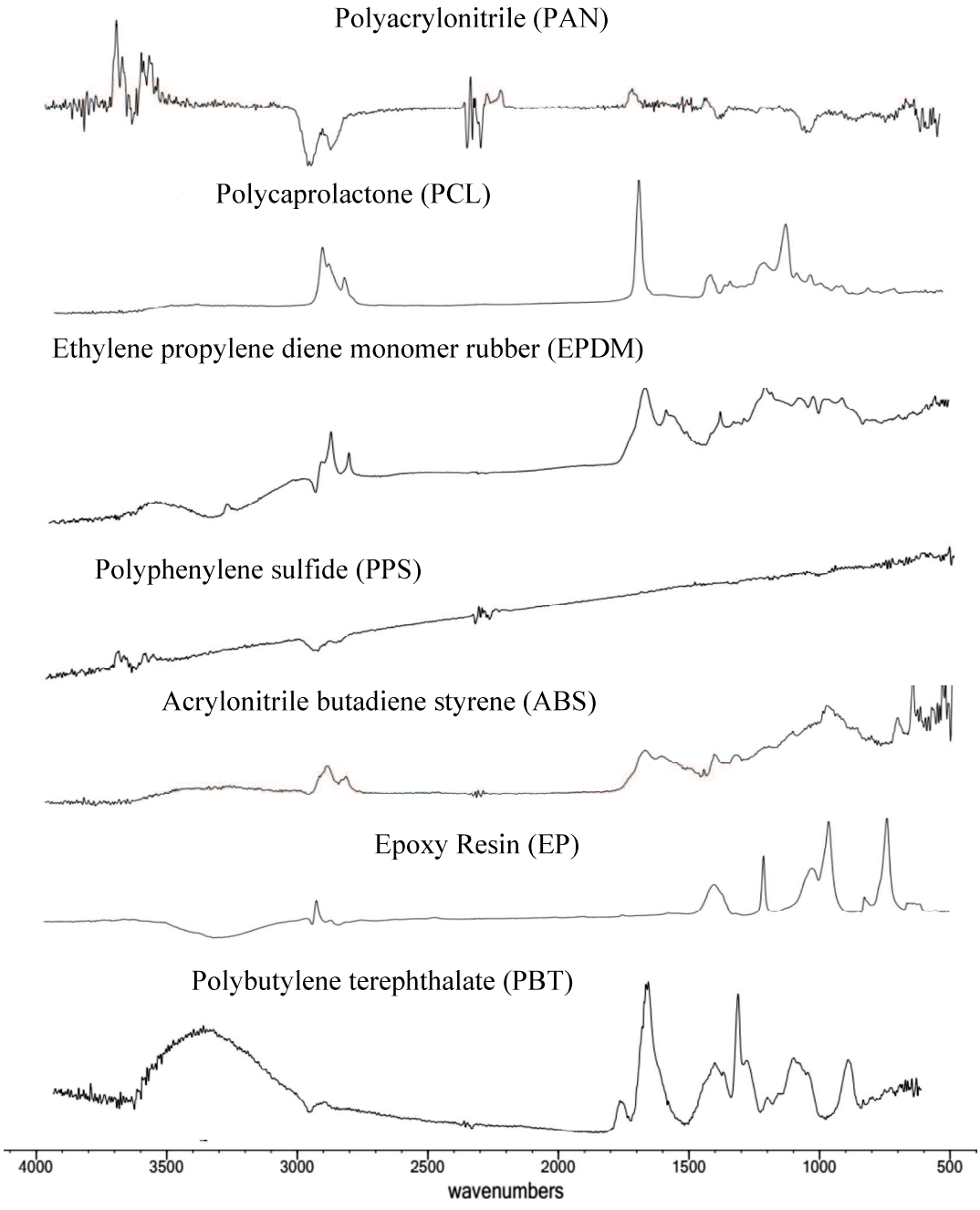


Fig. S3.5 ATR-FTIR Spectra for all the identified polymers

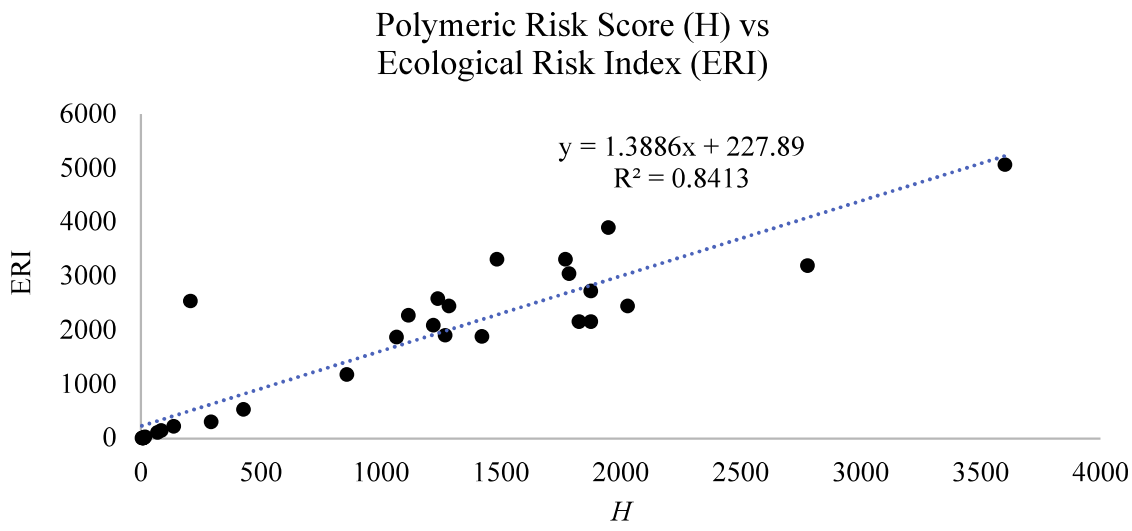


Fig. S3.6 Strength of relationship between the polymeric pisk score (*H*) and pollution risk index (*PRI*)

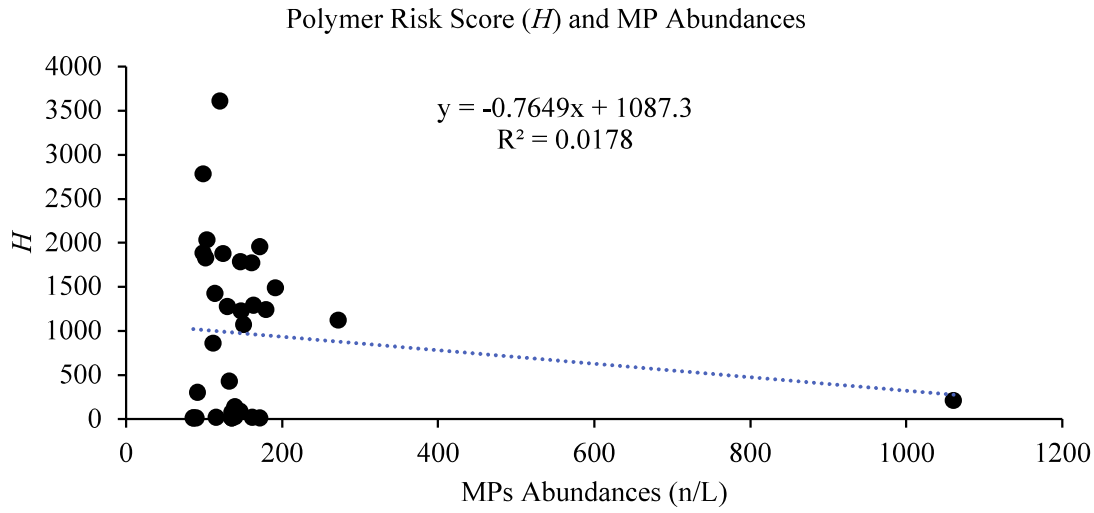


Fig. S3.7 Strength of relationship between the MPs abundances and polymeric risks scores

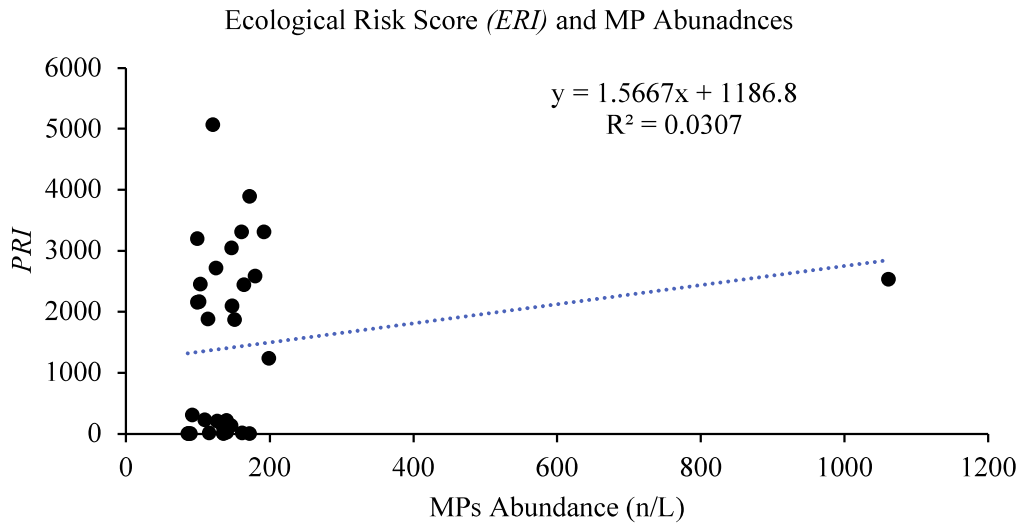


Fig. S3.8 Strength of relationship between the MPs abundances and pollution risks scores

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Chapter 4

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

This chapter assessed— MP pollution in the sediment of the small-scale Japanese rivers, the rivers as the sources-to-sink, and ecological risks. Overall, this study developed new insights into MP pollution in the small-scale river sediment with a focus of stated knowledge gaps identified in the previous study (Chapter 3) and in the Introduction part (Chapter 1).

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.

4.1. 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.

4.2. Materials and Methods

4.2.1. 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. 4.1). 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).

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. 4.1). The supplementary information (Table S4.1) 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.

4.2.2. 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.

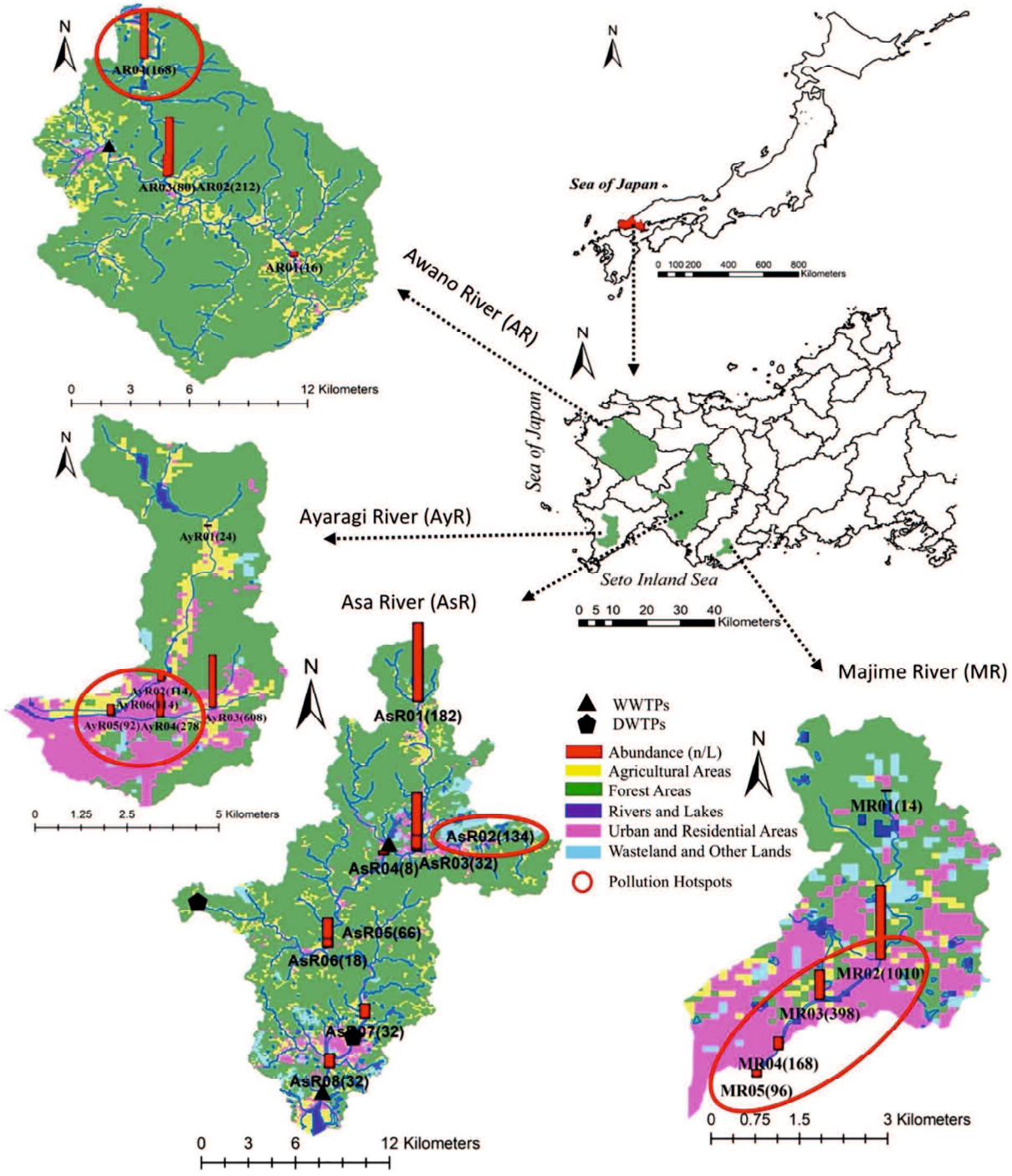

Fig. 4.1 Catchment land-use pattern, microplastic abundances, and risk levels along the Awano and Ayaragi (Sea of Japan-flowing) and Asa and Majime (Seto Inland Sea-flowing) rivers in Yamaguchi Prefecture, Japan. Red bars represent the MP abundances (n/kg). Red circles indicate MP pollution hotspots.

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).

4.2.3. 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).

4.2.4. 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. S4.1). 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.

4.2.5. 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.

4.2.6. 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 (*nth 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:

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

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

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 S4.2 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 (nth 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 nth root of the total ecological risk scores multiplied together.

4.2.7. Data Analysis

Microsoft Excel 2016 v.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.

4.3. Results and Discussion

4.3.1. 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. 4.2). Overall, the sediments of the four small-scale Japanese rivers are vulnerable to MP pollution.

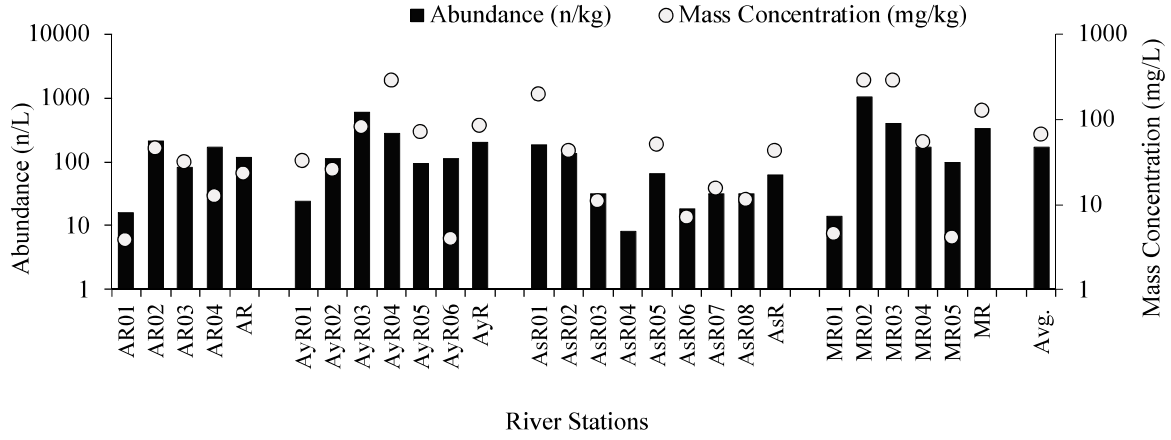

Fig. 4.2 Number-based abundances and mass concentrations of MPs and their distributions in sediments along the river stations.

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: 26.71 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. 4.1 & 4.2; Table S4.1). On the other hand, the abundances and distributions of MPs differed among the (up-, mid-, and down-) stream stations (Fig. 4.1 and 4.2). 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. 4.1 and 4.2). 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. 4.2). 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. 4.2; Table 4.1). 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. 4.3, 4.4 and 4.5; Table S4.2). 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. 4.2). 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.

4.3.2. MP Characteristics, Occurrences and Sources

4.3.2.1. Shapes, Sizes, Colors and Polymers

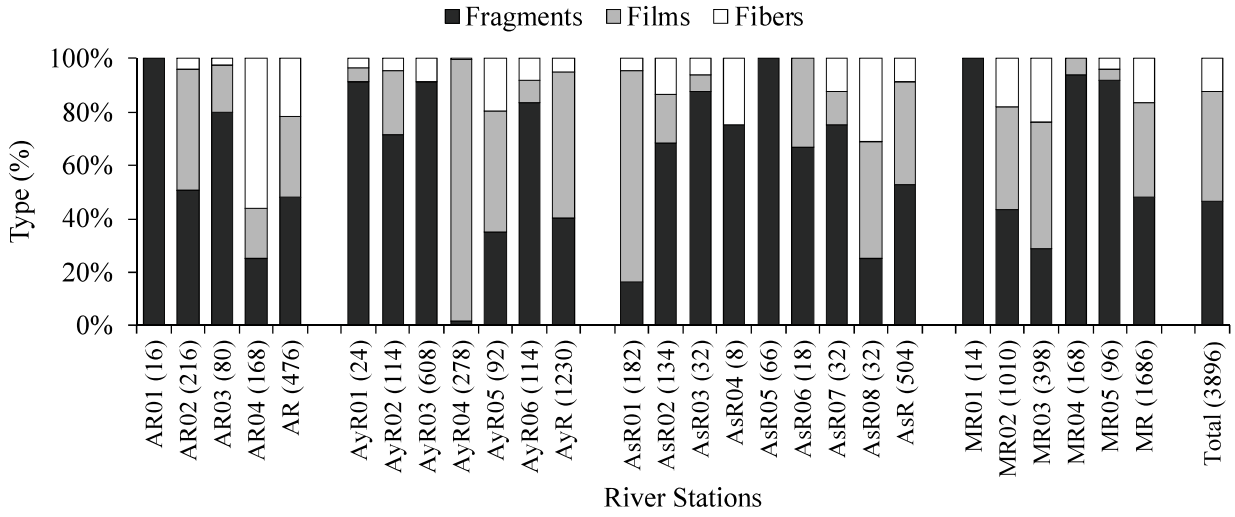

Fig. 4.3 Shape-based proportions of MPs of all the extracted particle numbers and their distributions among the river stations. Numbers in brackets represent the MP abundances.

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. 4.3 illustrates the shape-based MP distribution in the sediments along the river stations.

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. 4.4). The shape-size-based characterization exhibited that fragment MP particles were mostly SMPs, while the film and fiber MPs were LMPs (Fig. S4.2).

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. S4.3). Colorful MPs were observed with both bright and fresh, as well as dull and faded appearance.

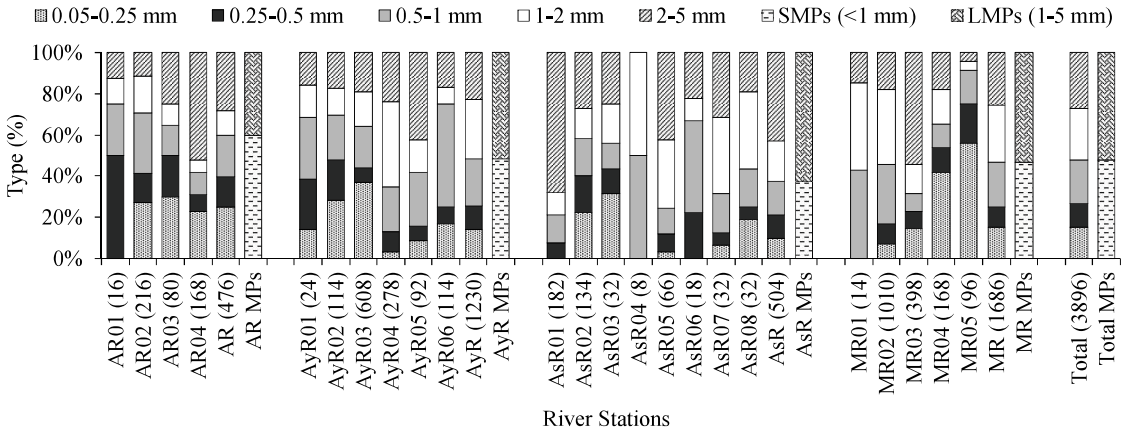

Fig. 4.4 Size-based proportions of MPs among all of the extracted particle numbers and their distributions among the river stations. All size ranges are in millimeters (mm). Numbers in brackets represent the MP abundances.

FTIR analysis revealed 16 different polymers (Fig. 4.5). 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) (3.44%), 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 S4.2). 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 S4.3). Fig. S4.4 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 AyR0; PBT in MR04–MR05; PCL in AR02).

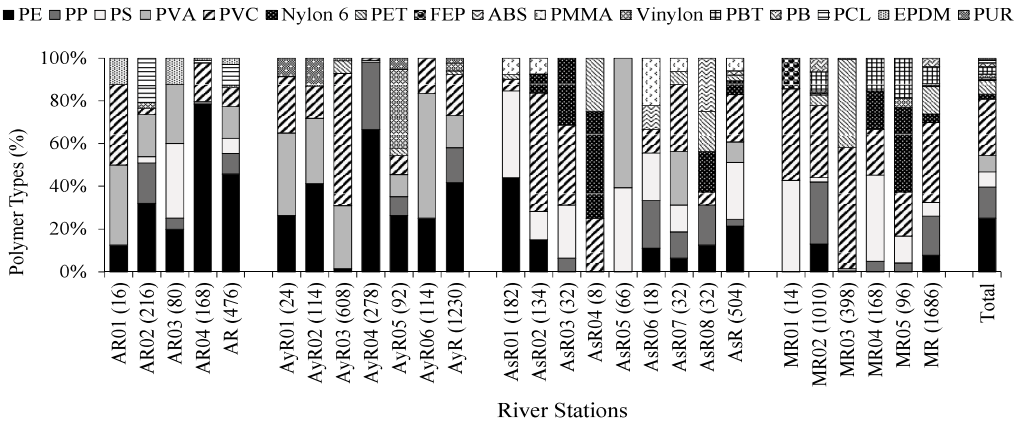

Fig. 4.5 Proportions of MP polymers among all of the extracted particle numbers and their distributions among the river stations. Numbers in brackets represent the MP abundances.

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. 4.1 & 4.5). This suggested that the land-use specific sources might influence the occurrence of similar and specific MP polymers prominently along the river stations (Fig. 4.5).

4.3.2.2 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. 4.5).

PVA and vinylon are polymers of the same monomer (Table S4.2). 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. 4.5). 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 S4.2).

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 S4.2. Overall, various land use-based point and non-point sources may contribute to the release of MPs.

4.3.2.3. 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 Yushan 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 4.1). 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 4.1 Summary of microplastics abundances and characteristics in 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

Table 4.1 Summary of microplastics abundances and characteristics in riverine environments worldwide (Continued)

Study Areas	Abundance (n/kg) (d. w.)	Concentration (mg/kg)	Major Characteristics	Refrefences	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—1320[a]		0.075–0.5	Fibers	PE, PVC, PS	Ding et al., 2019
Nakdong River, South Korea	1971±62[b]		0.02–0.3	Fragments	PP, PE	Eo et al., 2019
Antua River	18—629[a]	2.6—71.4	--	Fragments, Fibers	PE, PP	Rodrigues et al., 2018
Tibet Plateau Rivers	50—195[a]		<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

4.3.3. 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. S4.5). 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. 4.6). 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. 4.6). 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. 4.6). 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.

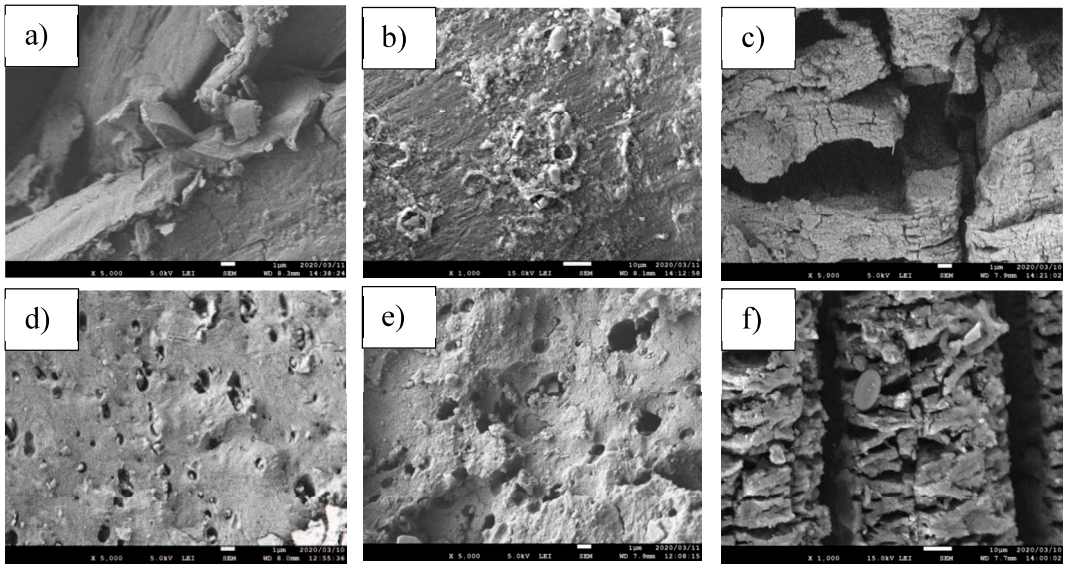

Fig. 4.6 Surface textures of the selected MPs by SEM-EDS analysis. a) PE fragment b) PE film c) PE fragment d) & e) PP fragment f) PE fiber

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. S4.6 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.

4.3.4. 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 fibers <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. 4.7). The dominance of high-density polymers in this study corroborates the results of several previous studies on river sediments (Table 4.1). 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. 4.5 and 4.7). 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 4.1). 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.).

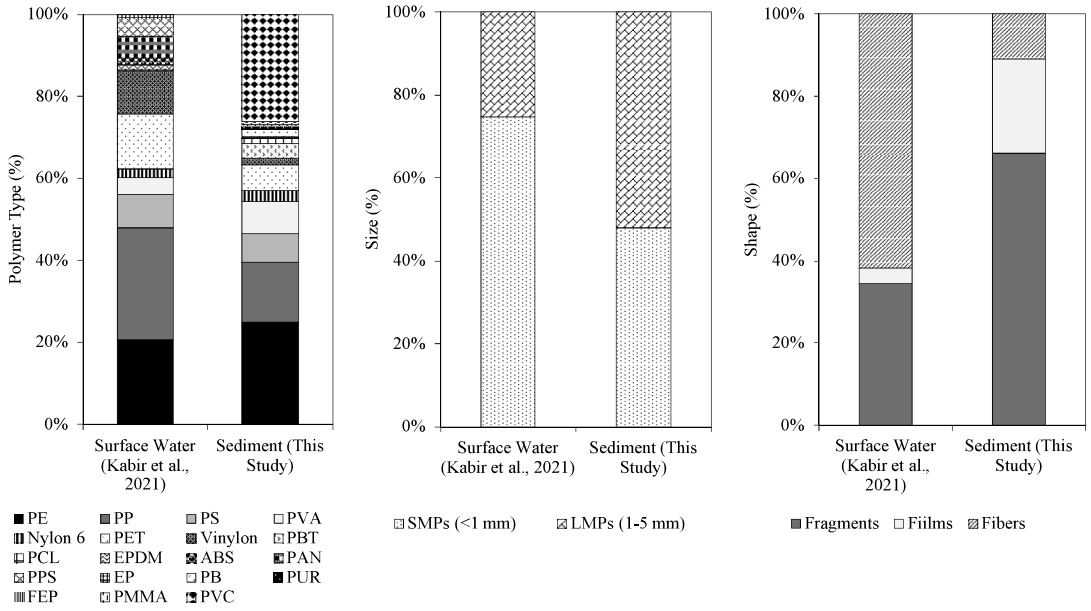

Fig. 4.7 Comparison of microplastic characteristics between the sediment and surface water of the small-scale Japanese rivers

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. S4.2). 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 S4.2). 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.

4.3.5. Comparison of Marine and River Microplastics

To understand the dynamics of MP pollution along the rivers and marine environments, we compared our study results among the marine and riverine environments. Considering the shape characteristics, we found similarities between the marine and riverine environmental matrices. Both the marine and riversurface water were dominated by fibers, and the marine and river sediments were dominated by fragments and films (Fig. 4.8). Thus, we found similar shape characteristics both in the marine end riverine environments. However, when considering the polymeric compositions, we found diverse polymers for the river environments than the marine environments. Overall, PE and PP were commonly dominant across the marine and river environments. Actually, PE and PP are dominant across the globe. This is due to their massive consumptions in all aspects. There were similarities in dominating polymers between river and marine surface water by the polymers— PE, PP and PET. However, there were dissimilarities in dominating MPs polymers i.e., PVC, between the river and marine environmental matrices. However, PVC was commonly found in the river sediments but not in the marine (Fig. 4.8). We speculated that the rivers were the initial sink to retain diverse MP polymers including the high-density PVC. And the Vinylon is related to PVA, the polymers of same monomers. Thus, overall we we found similar dominant and diverse polymers for the Japanese river and marine aquatic environments. This suggested that the rivers might affect the SIS and SJ marine systems as transporting the land-sourced MPs.

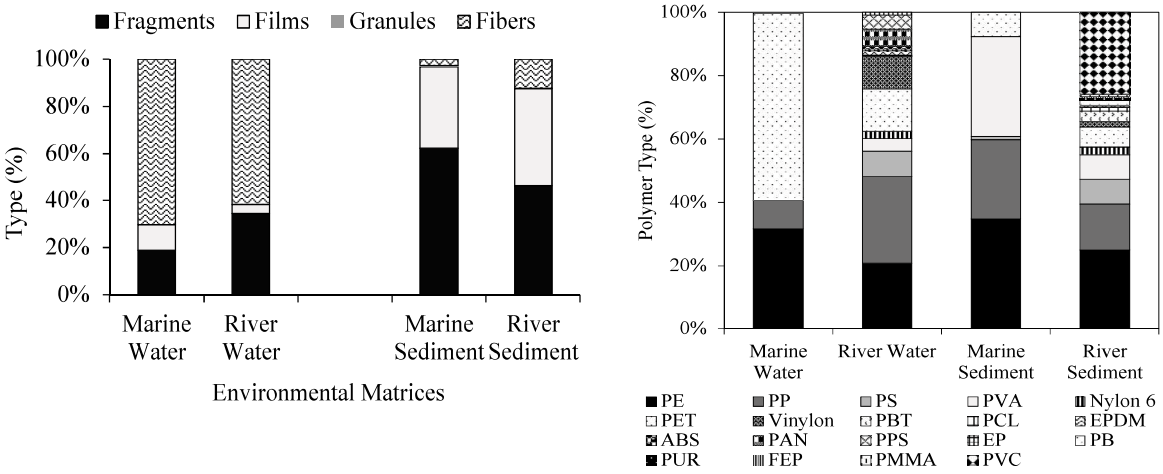

Fig. 4.8 Proportional comparison of MP shapes and polymers between the marine and river environments

To verify the influences of Japan land-sourced MPs being transported into the marine environments through the rivers, we compared the MPs between the SJ and SIS marine systems and the flowing rivers into them. The same dominant polymers (PE, PP, PET) between the river and marine systems were observed. The SIS falling rivers (AsR and MR) seemed to affect mostly the marine environment while comparing on the basis on polymeric abundances. However, while comparing the polymeric compositions in terms of

abundances, the similarities of dominant polymers were not observed clearly between the SJ and SJ falling AR and AyR rivers. The comparison between river water MP polymers to marine beach sediments, the results suggested that the SIS sediments might be affected by the rivers while the polymeric compositions and their abundances in SJ beach sediment showed a difference (Fig. 4.9). This suggested that the different sources also might affect the SJ seaside. According to our speculation earlier— the SJ might be affected by the other marine areas as well as the Japan land-sources, while the SIS might be affected by the Japan land-sources mainly. The MPs are getting emitted by the Japanese rivers, this verified our hypothesis preliminarily that SIS might be affected by the Japanese rivers while SJ might be affected by the MPs originated from other land-sources alongside the Japan land-sourced MPs. Thus, the influences of Japanese rivers on the SJ might not be observed clearly. River MPs of PE, PP and PET might be deposited in the beach sediment to and around the river mouths. We already thought rivers were prominent initial sink to retain the land-sourced MPs, thus, the Japan-land sourced MPs were retained in river sediments initially. The schematic diagram Fig. 4.10 shows the flow of MP polymeric compositions from the land-sources to sinks (land-sources-to-river-to-marine).

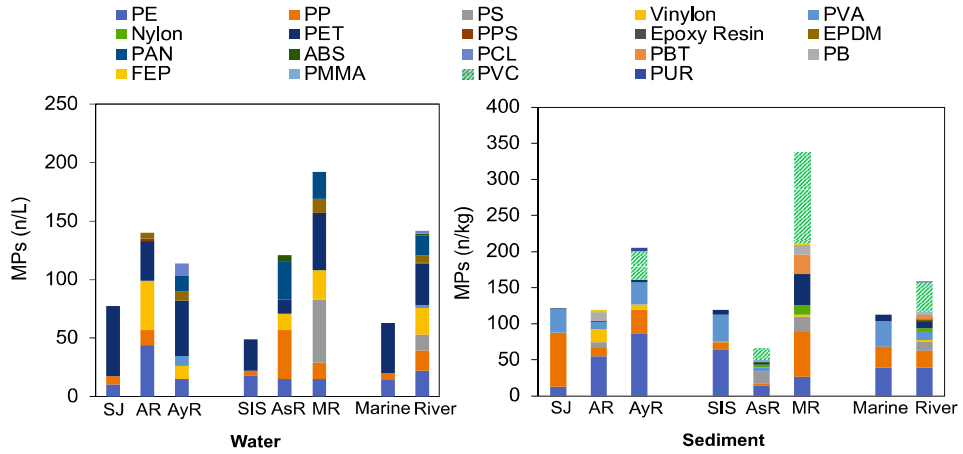

Fig. 4.9 Comparison of MP polymers and their abundances along the marine and riverine environments. The values were normalized per 'liter' and 'kg' for each site.

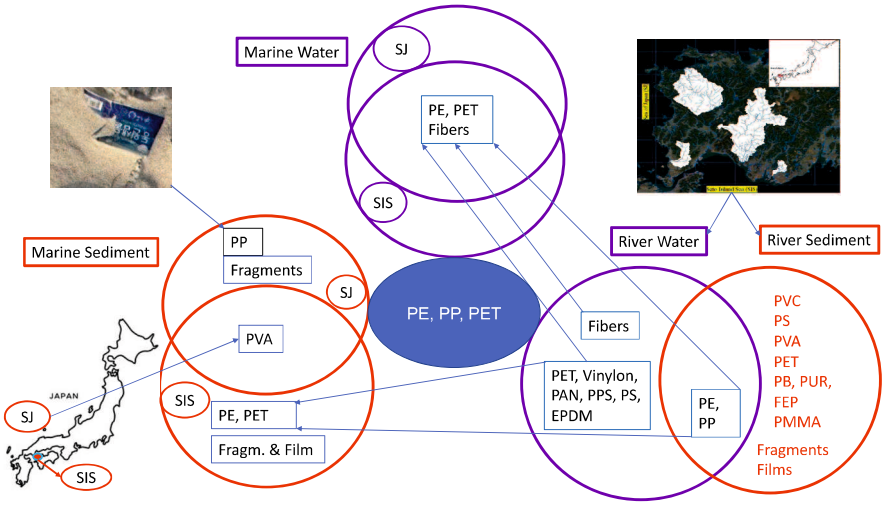

Fig. 4.10 A schematic diagram of sources-to-sink phenomena showing MPs flow from land-sources and their fate into the marine and rivers

4.3.6. 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. 4.11). 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 4.2 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. 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. 4.11; Table 4.2). 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. 4.5 and 4.11). 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 S4.2). 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. 4.1 and. 4.5).

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. 4.11; Table 4.2). 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 4.2). 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. 4.11). 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 S4.2). This ecological risk assessment model can be utilized to assess the ecological risks for any ecosystem.

Table 4.2 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

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 (AR01–03, 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. 4.11). 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. 4.1 and 4.11). 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. 4.1). 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. 4.1 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.

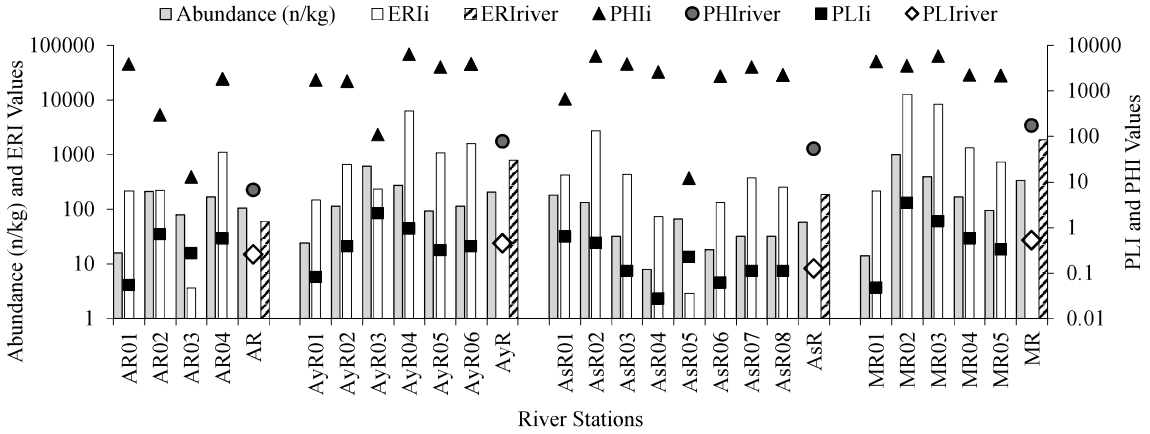

Fig. 4.11 Microplastic abundances, pollution load index (*PLI*), polymeric hazard score (*PHI*), ecological risk value (*ERI*), and their distributions among the river stations.

4.4. 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. Urban and residential land-use sources might release higher numbers of MPs than non-point sources at the river catchment scale. Furthermore, sediment MPs underwent weathering processes and vectored metal contaminants, which are potential to cause synergistic hazards to these riverine ecosystems. The high-density MP polymer types 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. Overall, MP characteristics in sediments differed from surface water compartments in terms of shape, size, and polymer type. A comparison of riverine and marine MPs suggested that the similar shapes-polymers were dominant for both the environmental compartments except the PVC dominance in the riverine sediments. River sediments retained diverse MPs including the high-density PVC. Thus, rivers acted as the primary sink for Japan's land-sourced MPs. In addition, the comparison results of polymeric abundances between the riverine and

marine MPs suggested that the Japanese rivers might affect mainly the SIS as the pathways of sources-to-sinks. In this comparison, this couldn't be observed clearly that the Japanese rivers might affect the SJ seaside. In the study of Chapter 2, we thought that the MP compositions in the marine beach sediment of each sea were different because of the difference of the sources. It was speculated that the SIS might be affected by the Japan land-sourced MPs, and the SJ was thought to be affected both by the Japan land-sources as well as the regional territory. This comparison preliminarily verified the speculation from our previous studies. Further investigations are required regarding environmental factors and processes influencing the deposition mechanisms of MPs in river sediments, as well as the flow and transportations processes of MPs into the marine realm through the river pathways.

An assessment of ecological risks exhibited a risk level from low to very high. High ecological risk was linked to MP abundance and the presence of toxic polymers. Both point and non-point sources might emit toxic polymers; however, mostly urban and residential land-use point sources pose high ecological risks due to the release of higher numbers of MPs and toxic polymers. Thus, urban areas and a higher number 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. The river water-sediment interfaces of small-scale Japanese rivers are vulnerable to ecotoxicological threats.

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 riverine ecological toxicity. 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.

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Supplementary Material

Table S4.1 River basin and land-use information of the studied rivers

	Area (km^2)	Population (Density/km^2)	Urban	Agriculture	WWTPs	Forest	Others*
Awano River (AR)	177.02	26.71	1.51 (0.85%)	23.32 (13.17%)	1	149.88 (84.67%)	2.31 (1.31%)
Ayaragi River (AyR)	19.78	657.23	0.97 (4.89%)	2.18 (11.04%)	—	15.69 (79.35%)	0.93 (4.71%)
Asa River (AsR)	231.81	115.75	10.68 (4.61%)	27.11 (11.69%)	2	179.22 (77.31%)	14.80 (6.38%)
Majime River (MR)	12.34	1121.15	3.31 (26.83%)	0.75 (6.11%)	—	6.66 (53.95%)	1.62 (13.11%)

*Others including- athletic field, an airport, a racetrack, a baseball field, a school harbor area, an open space in an artificial land, etc.

Table S4.2 Identified polymers, their monomers, density, uses and applications, and risk scores

Polymers	Abbreviations	Monomer	Density	Applications	Observed Shapes	Risk Score (S_n)*
Polyethylene	PE	Ethylene	0.91–0.96	Reusable bags, trays and containers, agricultural firm, food packaging film, toys, milk bottles, shampoo bottles, pipes, houseware (Plastics Europe, 2019)	Fragments, Films, Fibers	11
Polypropylene	PP	Propylene	0.85–0.94	Food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, automotive parts, bank notes, etc. (Plastics Europe, 2019)	Fragments, Films, Fibers	1
Nylon 6		ε-caprolactam	1.14–1.15	Textiles, packaging, engineering, medical, and agriculture for having UV absorption capacity (Hu and Yang, 2000)	Fragments, Fibers	50
Vinylon		Vinyl acetate	1.19	Japanese Traditional Dresses, Working Wear, Fishing Nets, seaweed farming nets, Ropes, Filter Cloth, Canvas, Sheets, Cement Reinforcement Material, Hoses, Belts, Tire Cords, Kanreisha (Open Thin Fabric), Threads for Tatami Mats, Construction Nets, Paper Making Felts, etc. (JCFA)	Fibers, Films	1
Polyethylene Terephthalate	PET	Ethylene Glycol	1.38	Bottles for water, soft drinks, juices, cleaners, textiles (Plastic Europe, 2019)	Fibers, Fragments	4
Polystyrene	PS	Styrene	0.96–1.05	Food packaging (dairy, fishery), building insulation, electrical & electronic equipment, inner liner for fridges, eyeglasses frames etc. (Plastic Europe, 2019)	Fragments	30
Ethylene propylene diene monomer	EPDM	Ethylene, propylene, and diene comonomer	1.3	Synthetic rubber roofing membrane automotive and construction industries, electrical, tire (Holden, 2017)	Fragments, Films	N C
Polybutylene terephthalate	PBT	Dimethyl terephthalate	1.30	Packaging, automotive, electrical, and consumer markets, optical fibers (Plastics Europe, 2019).	Films	N C
Polycaprolactone	PCL	ε-caprolactone	1.145	Scaffolds in tissue engineering, microparticles for drug delivery, making trash bags, microelectronics, adhesives, and packaging (Labet and Thielemans, 2009).	Films	N C
Polyvinyl Alcohol	PVA	vinyl acetate	1.19	Industries, such as textile, paper industry, and food packaging industry (Satoh, 2014).	Fragments	1
Acrylonitrile Butadiene Styrene	ABS	Styrene	1.02–1.08	Automotive applications, pipes, toys, electrical, households, 3D printing etc. (Begum et al., 2020; McKeen, 2018)	Fragments	6552
Polyvinyl chloride	PVC	Vinyl chloride	1.16–1.58	Building and constructions, electrical/electronic uses pipes, floor coverings, cable insulation, roofing sheets, packaging foils, bottles, medical products, water supply distribution systems, medical applications, food packaging, industrial hoses, gaskets, elastic automotive parts, electrical cable covers etc.	Fragments, films	
Fluorinated ethylene propylene	FEP	Ethylene propylene	2.1–2.3	Cables for chemical platoon heating tapes foils filaments and cables at coating for valves, tubes, vessels and tanks electrical applications as terminal blocks and valve and tube holders. non-stick applications in food processing	Fragments, Films	N C
Polyurethane	PUR	Propylene oxide	1.2	Polyurethane apparel- manmade skin and leathers, garments, sports clothes, sports shoes common sports equipment (soccer balls, judo mats, and binders on running tracks sports flooring) major appliances, rigid foams for refrigerator and freezer thermal insulation systems, car seats, bumpers, interior "headline" ceiling sections, car bodies, spoilers, doors, and windows, household floors, flexible foam padding cushions, buildings and constructions, surface coatings, adhesives, solid plastics, and athletic apparel, resilience foam seating, wheels and tires (such as escalator, shopping cart, elevator, roller coaster and skateboard wheels). biomedical devices (grafts, catheters, artificial arteries, heart valves, sutures, bandages, etc.)	Fragments	13844
Polybutene	PB	1-butene, 2-butene, and isobutylene	0.95	Personal care products, cosmetics, automotive sealants, adhesives, extenders for putties used for sealing roofs and windows, coatings, polymer modification, agricultural films, coatings etc.	Fibers	N C
Polymethyl methacrylate	PMMA	Methyl methacrylate	1.18	Medical materials, cosmetics, biomaterial applications such as bone cement, lenses, bone substitutes, and drug delivery systems, lighting, aircraft glazing, contact lenses, and others (Avella et al., 2001a)	Fragments, Films	1021

* The risk scores are taken from Lithner et al., 2011.

Table S4.3 Shape-color-polymer characteristics of the identified microplastics

	Transparent	White	Blue	Green	Red	Yellow	Grey	Black
Fragment	PVA, ABS, PVC, Nylon 6	PVA, PVC, PS	PE, PVC, PP, PBT	PVC, PE, PUR	PVC, PS, PMMA	PMMA	PE, PVA FEP	PVC, PE
Film	PE, PP	PE, ABS, PP	PE	PCL, PP, PMMA	PVA, PVC, PMMA	Vinylon	PE, EPDM, PCL, FEP	PE, PET
Fiber	Vinylon, PP, PE, PET	PE, Vinylon	Vinylon, PE	PP, Nylon 6, PB				

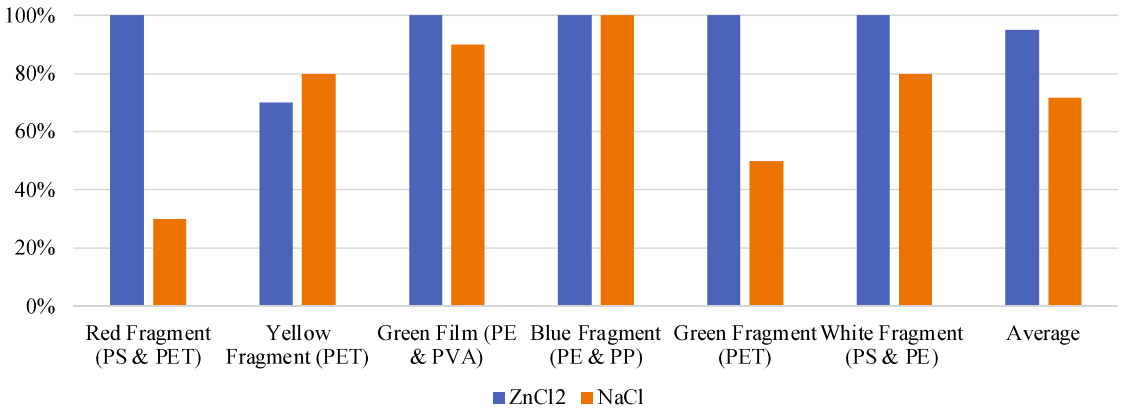


Fig. S4.1 MPs extraction efficiency by the $ZnCl_2$ (1.5 g/cm^3) and NaCl (1.2 g/cm^3) density separation solution

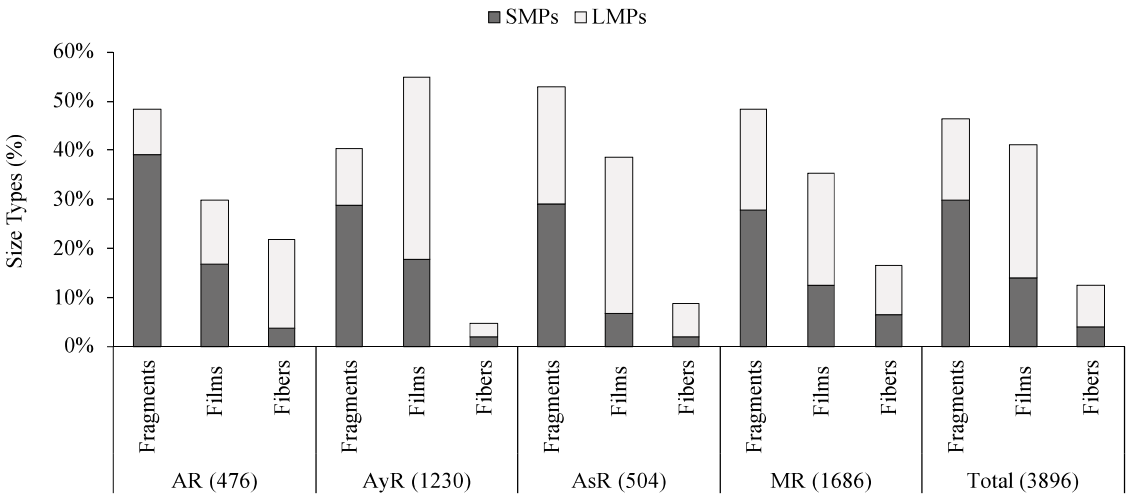


Fig. S4.2 Shape-Size based proportions of MPs among all of the extracted particle numbers and their distributions among the rivers. Numbers in brackets represent the MP abundances.

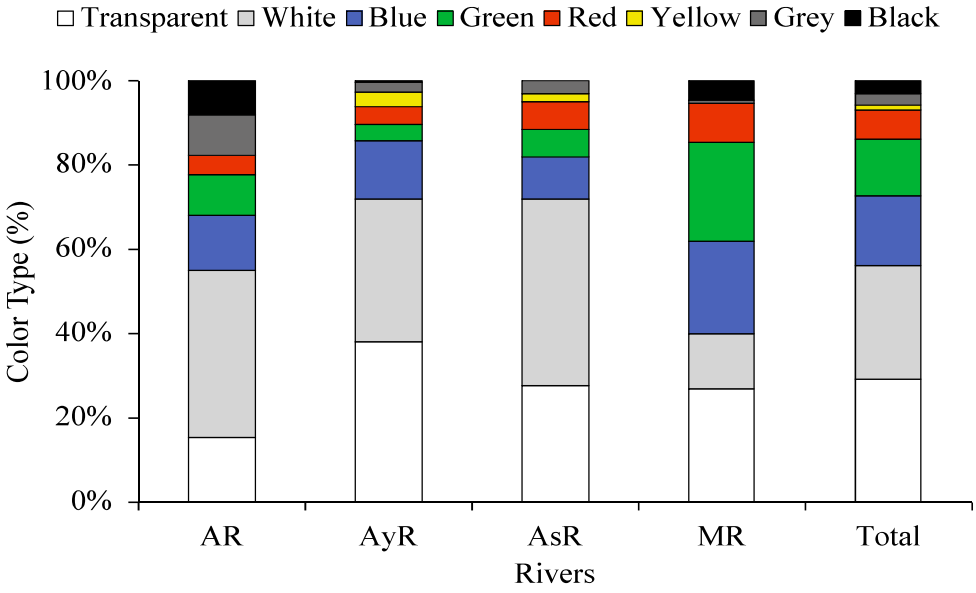
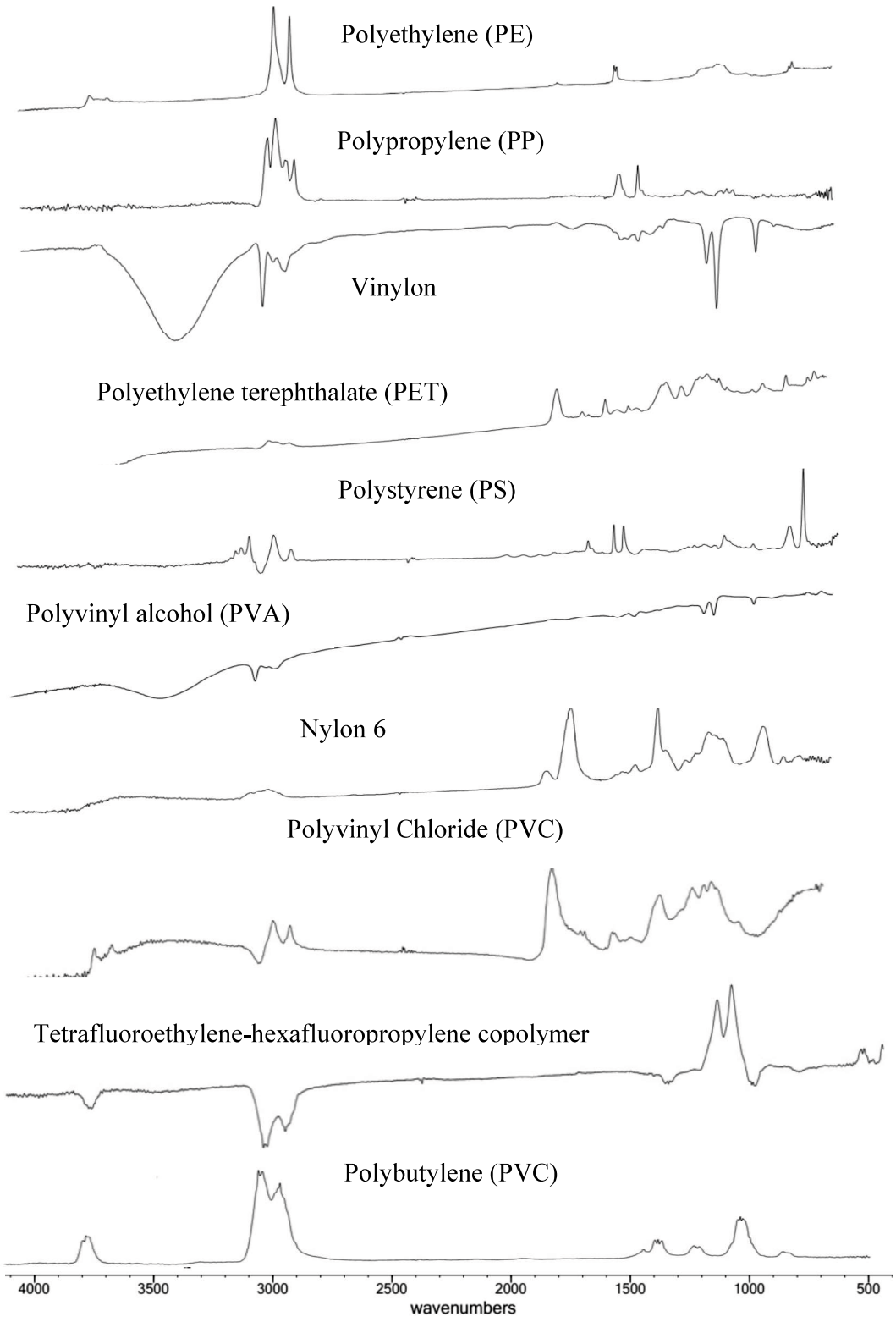


Fig. S4.3 Color based MPs distributions along the rivers


Polyethylene (PE)
Polypropylene (PP)
Vinylon
Polyethylene terephthalate (PET)
Polystyrene (PS)
Polyvinyl alcohol (PVA)
Nylon 6
Polyvinyl Chloride (PVC)
Tetrafluoroethylene-hexafluoropropylene copolymer
Polybutylene (PVC)
4000
3500
3000
2500
2000
1500
1000
500
wavenumbers

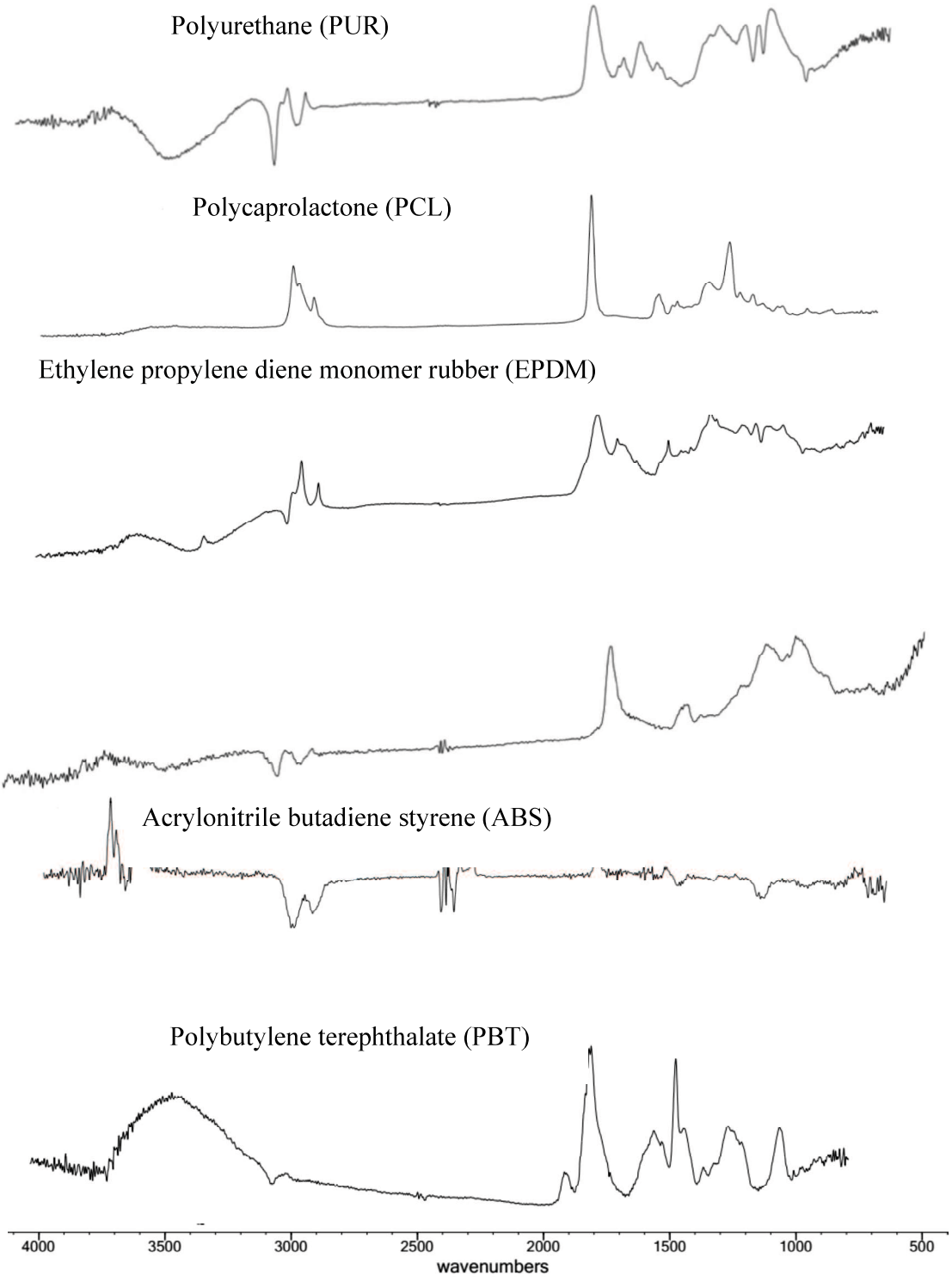


Fig. S4.4 ATR-FTIR Spectra for all the identified polymers

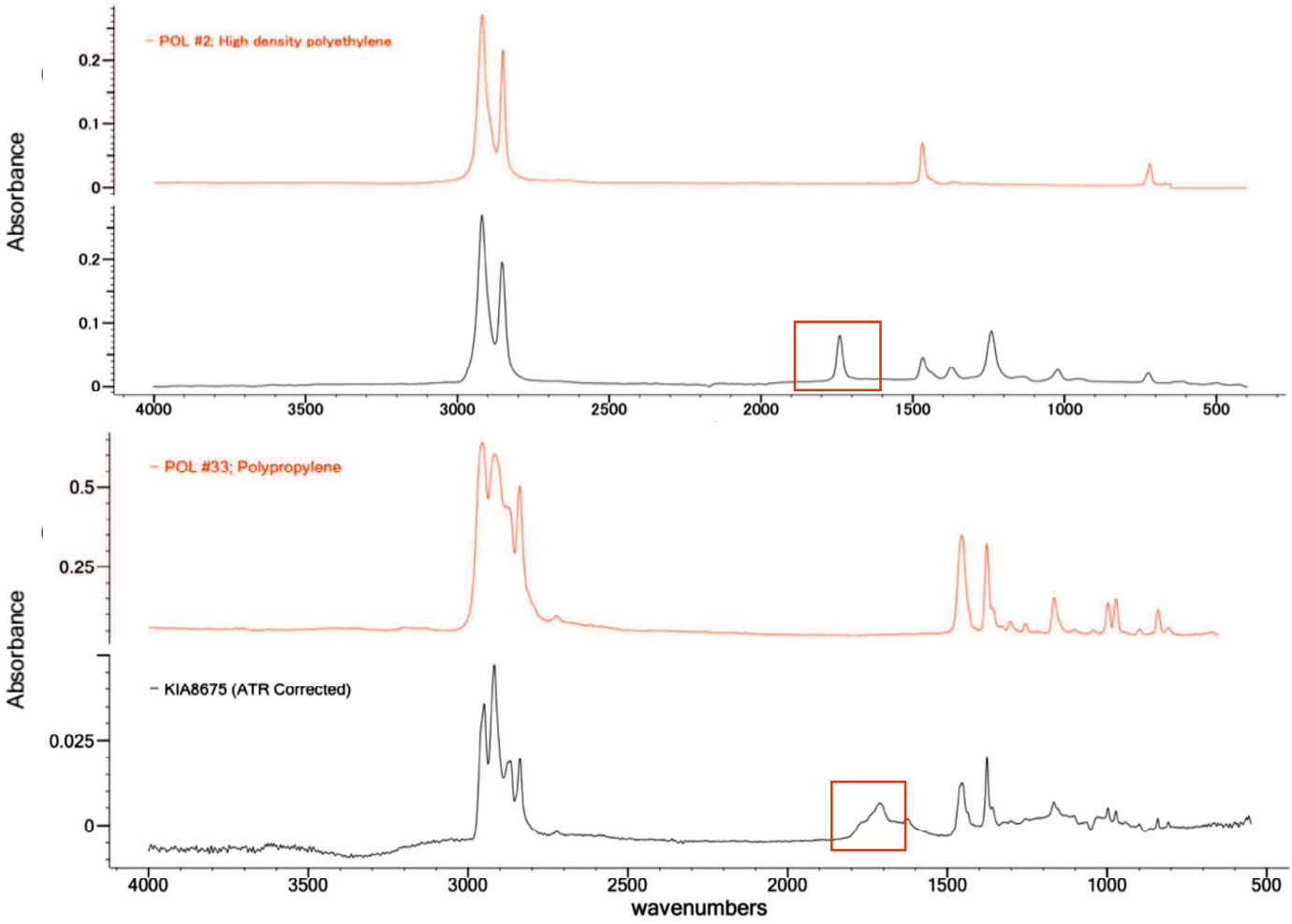
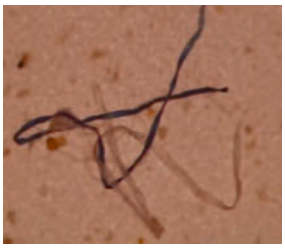
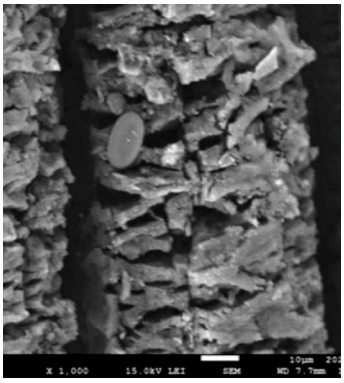
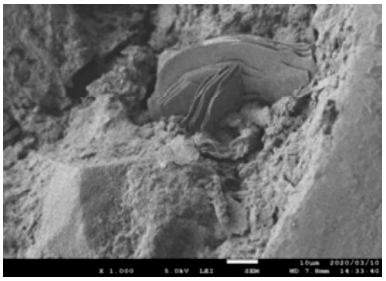
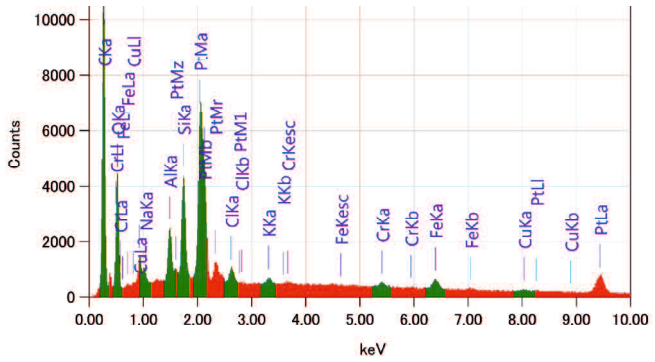


Fig. S4.5 FTIR spectrum having the presence of carbonyl group indicating the chemical weathering of MPs. Red box indicates the presence of carbonyl group in the FTIR spectrum.








Counts
keV
CKa
FeLa
CuLl
OKa
FeLl
CrLl
CrLa
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CuLa
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SiKa
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PtMb
ClKa
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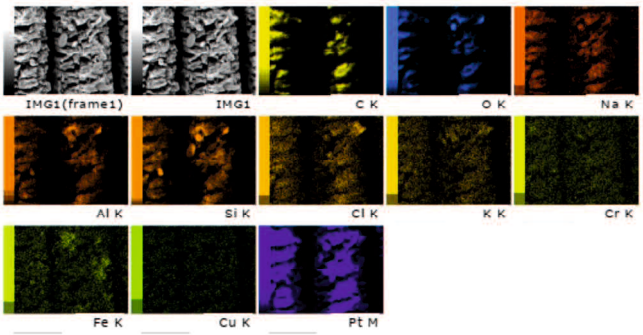
PtLa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O K
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Cl K
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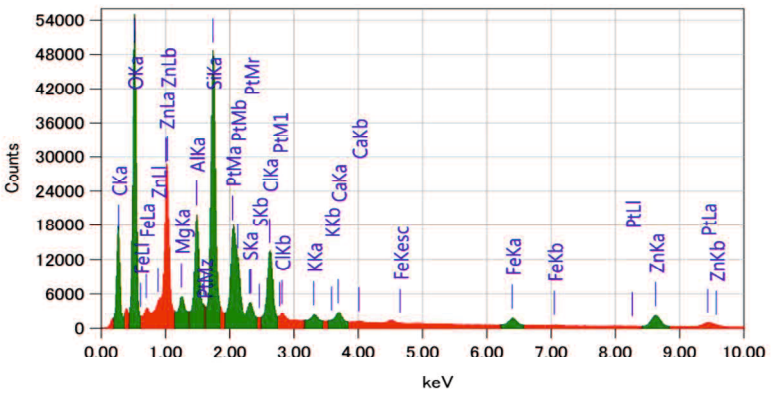
Pt M


Counts
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OKa
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SKa
SKb
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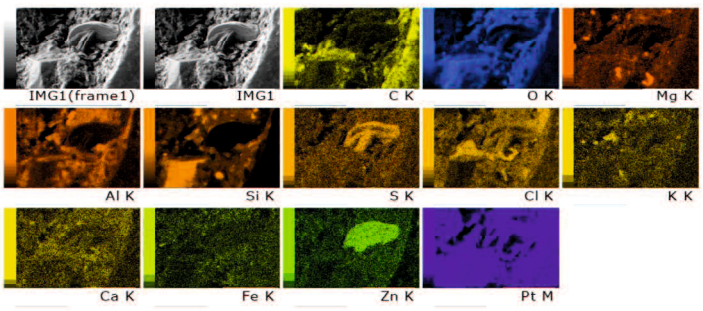
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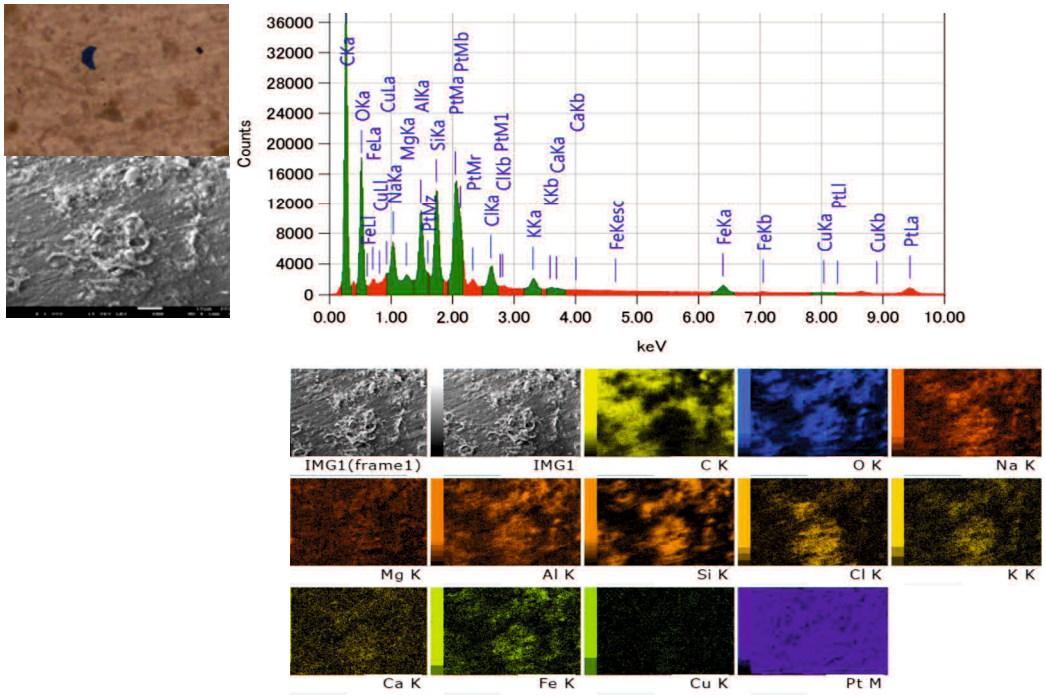

Fig S4.6 Mapping of elemental composition on examined microplastic surfaces

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Chapter 5: Summary and Recommendations

5.1. Summary

For the first-time, microplastic pollution along the SIS and SJ coastal areas in the prefecture were explored in this research. High-level pollution was found in comparison to other marine environments worldwide. The microplastic types (shapes-sizes-colors-polymers) were different both in environmental matrices (marine water and sediments) and spatial scales (SIS and SJ areas). Small microplastic fragment particles (<1000 μm) dominated sediment and large microplastic fibers (1000-5000 μm) were major in water along with the diverse polymers. Sediments were more polluted than water which might be due to complex biophysical reasons. According to the field observation, it was likely that the Japan land-sources might affect the SIS while the regional territory might affect the SJ through transboundary fluxes of (micro-)plastics alongside the domestic sources. Overall, microplastic pollution assessment results indicated threats to these marine ecosystems. Thus, this study opened the ways for further studies towards the pathways of microplastic pollution sources-to-sinks.

While studying source-to-sink pathways, this study discovered that small-scale Japanese rivers were highly polluted with microplastics compared to reported larger rivers around the world. This appeared to be the first study filling the literature gaps about small-scale river microplastic pollution. Microplastics characterization revealed that particles <1000 μm in size, fibers and fragments, and diverse polymers were dominant in river surface water. A new dominant polymer 'Vinylon' was identified. This polymer was invented in Japan and is being commonly used in industries, agricultures, fisheries etc. We were first to identify and report it. Both the point and non-point sources might release microplastics in the riverine water environments. Apart from this, the small-scale rivers acted as the key transportation pathways responsible for SIS and SJ marine pollution emitting billions and tons microplastics sourced from Japan lands. Though the river basins were small at size, they were highly important in generating microplastics and influencing marine pollution.

In contrast, rivers were not the linear pathways to release them in the marine realm. Microplastics are retained in the riverine sediments. The abundance comparison revealed that the sediments of small-scale Japanese rivers were MPs polluted relatively at a medium level compared to other rivers around the world. Large particles (>1000 μm), fragments and films, high-density polymers dominated in sediments which were different from surface water compartmental microplastics. The findings indicated that the microplastic particle characteristics (high-density, shapes and sizes), as well as the environmental factors (weathering, biofouling, river hydrodynamics and geomorphology etc.) might affect their retention in the river sediments. The point sources i.e., the urban and residential land-use influenced the occurrences of microplastics and might be the major sources of the pollution in the river sediment environments. Through the observation of surfaces of the microplastics, it was found that the river sediment microplastics underwent weathering processes and contained metal contaminants onto their surfaces which could pose synergistic hazards to the riverine ecosystems.

Overall, the rivers were the initial sink and SIS and SJ were final sink of land-sourced microplastics. The riverine studies on microplastic pollution filled preliminary knowledge gaps within river and marine environments; land-use sources and occurrences; fate, and emission of microplastics to the marine systems being carried out by the rivers as the sources-to-sinks phenomena.

What's more, the questions— what ecological risks of the pollution were applicable to aquatic ecosystems remained unknown to date. Despite the microplastic abundances reported widely, knowledge of ecological risks remained unknown. To address ecological risks and contribute to ecological risk assessment methods, we developed risks assessment formulae. Employing the risks assessment models and ecological risk index criteria, the ecological risks of microplastic pollution were found variably low to high for the riverine environments. This study empirically derived that, 'the higher were the abundances of microplastics and toxic polymers, the higher were the pollution levels and risks' at any particular ecosystem. Mainly, the urban and residential areas dominated river downstream areas ranked high ecological risks of microplastic pollution in the fluvial settings. As well as providing the insights about the presence of highly toxic polymers and higher abundances of microplastics in the water and sediment compartments with an implication of riverine ecological toxicity, the ecological risk levels also reflected the influences of human activity in generation of higher amounts of microplastics and highly toxic polymers, their release into riverine environments, and causing pollution hotspots. Overall, the ecological risks provided a baseline for future comprehensive assessments and developing practical approaches towards setting environmental quality monitoring criteria, the pollution control, management, and risks reduction.

In fine, this doctoral research developed new insights into microplastic pollution— i. addressed knowledge gaps in microplastic pollution occurrences within marine and freshwater systems; ii. filled the knowledge gap about small-scale rivers; iii. identified a new abundant polymer in Japan; iv. investigated prominent sources-to-sinks in Japan; v. developed ecological risk assessment formulae, assessed the risk levels, and identified pollution hotspots. This dissertation will contribute towards environmental quality criteria setting and future monitoring of microplastic pollution, as well as developing practical approaches towards the pollution control and management for Japan and beyond in light of the popular philosophy "thinking globally and acting locally".

5.2. Recommendations

Based on the findings in this study, we recommend filling the following knowledge gaps and solve the complex microplastic issues following—

- To conduct the comprehensive land-use sources assessment at the riverine and marine catchment scales to facilitate the control at sources as part of the pollution management.

- To assess the microplastic pollution and plastic additives (in correlation with microplastics) associated risks to biota and human, develop a risk framework applicable to exposure to human and biota, and evaluate the socio-ecological dimensions of the pollution risks in the context of human-biophysical entities.

- To develop practical approaches to control, mitigation, management, and risks reduction of microplastic pollution.