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IMPACT OF GREATER PARIS MEGACITY ON THE ABUNDANCE AND FATE OF SMALL MICROPLASTICS IN THE SEINE RIVER

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Thèse soutenue le 17 décembre 2025, par

Cleo Ninja STRATMANN

Composition du jury :

Rachid AMARA Professeur, Université du Littoral	*Président*
Alexandra TER HALLE Directrice de recherche, Université Paul Sabatier	*Rapporteuse*
Elodie GUIGON Maîtresse de conférences, HDR École pratique des hautes études	*Rapporteuse*
Rachid AMARA Professeur, Université du Littoral	*Examinateur*
Bruno TASSIN Directeur de recherche, École nationale des Ponts et Chaussées	*Directeur de thèse*
Johnny GASPERI Directeur de recherche, Université Gustave Eiffel	*Co-Directeur de thèse*
Rachid DRIS Maître de conférences, Université Paris-Est Créteil	*Encadrant*

DOCTORAL THESIS

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Cleo Ninja STRATMANN

Doctoral school of Science, Engineering and Environment, ED SIE

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The following institutions and programmes participated in the conduction of this PhD thesis:



Artist: M. Schulmeister-Kielblock

Cleo Ninja Stratmann, née Sabrotzky

EDUCATION

2020 – 2025	PhD Environmental Science and Technology École des Ponts ParisTech, Institut Polytechnique de Paris, Université Paris Est Créteil, France
2012 – 2016	Master of Science Technical University Berlin, Germany
2007 – 2012	Bachelor of Science Technical University Berlin, Germany

DISSEMINATION AND COMMUNICATION

Mar 2023
UNESCO – EU H2020 LimnoPlast conference, Paris, France
Microplastics > 25 µm in the Seine River (Oral & Poster)

May 2023
SETAC Europe 32nd Annual Meeting, Copenhagen, Denmark
Investigating Microplastics > 25 µm in the Seine River (Oral)

Dec 2022
Netherlands Centre for River Studies – science day, Wageningen, Netherlands
Better together – Reducing barriers on plastic research with the Plastiverse (Keynote Oral)

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PIREN-Seine science day, Paris, France
Microplastic >25 µm in the Seine River (Oral)

Jan 2022
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Other contributions:

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Cleo Stratmann

Trondheim, Norway, 31 October 2025

ENGLISH SUMMARY

With plastic pollution comes the modern challenge of microplastic (MP) contamination. MPs are pollutants that affect freshwater environments, with rivers as receiving environments and transport pathways. Urban agglomerations play a key role in MP release to rivers with a variety of potential sources. To advance the understanding of MP pollution in urban rivers, this thesis investigated MPs in the Seine River in Greater Paris. In a one-year field monitoring study (2021–2022, chapters 3 and 4), upstream and downstream MP abundances were measured up to 4,700 particles m^{-3} revealing strong spatiotemporal variability linked to hydrological regime, precipitation, and urban discharges. A MP mass balance indicated that urban discharges such as wastewater treatment plant (WWTP) effluent and combined sewer overflows (CSOs) are important contributors to riverine MP pollution. The MP load increased from upstream to urban sites, indicating an urban effect with temporary MP retention in the urban center and periodical peaks in downstream transport. In a complementary study (chapter 5) two sampling methods (sediment trapping and *in-situ* pump filtration) were compared under field conditions. The study demonstrated that methodological choices influence the measurement of MP concentrations and polymer types. Both methods yielded similar patterns of MPs across sampling days and similar particle sizes but showed differences in polymer diversity. These results emphasize a need for harmonized field methods and transparent reporting to improve data comparability. Overall, the findings highlight the complexity of MP fate in dynamic urban river systems and provide new knowledge that can be used to inform and improve future monitoring, modeling, and management strategies.

Keywords:

Microplastics, Seine river, urban pollution, field monitoring, microplastic mass balance

RESUMÉ EN FRANÇAIS

La contamination par les microplastiques (MP) est une conséquence de l'usage généralisé de la matière plastique. Les MP constituent des polluants affectant les milieux d'eau douce, en particulier les rivières qui jouent à la fois le rôle de milieux récepteurs et de voies de transport. Les agglomérations urbaines occupent une place majeure dans les rejets de MP vers les milieux fluviaux, en raison de l'intensité et de la diversité des sources qu'ils peuvent concentrer.

Afin d'améliorer la compréhension de la pollution par les microplastiques dans les rivières urbaines, cette thèse a étudié leur présence et leur dynamique dans la Seine, au sein de la région métropolitaine du Grand Paris. Dans le cadre d'un suivi de terrain d'une durée d'un an (2021–2022, chapitres 3 et 4), les abondances de MP mesurées à l'amont et à l'aval de l'agglomération parisienne ont atteint jusqu'à 4 700 MP.m^{-3}, révélant une forte variabilité spatio-temporelle liée à l'hydrologie, aux précipitations et aux rejets urbains.

L'établissement d'un bilan massique des microplastiques a montré que les déversements urbains, notamment ceux issus des stations d'épuration (WWTPs) et des déversoirs d'orage (CSOs), constituent des contributeurs majeurs à la pollution fluviale. La charge en microplastiques augmente de l'amont vers les zones urbanisées, traduisant un effet urbain marqué, avec une rétention temporaire des particules dans le centre métropolitain et des pics périodiques de transport vers l'aval.

Dans une étude complémentaire (chapitre 5), deux méthodes d'échantillonnage (trappes à sédiment et filtration *in-situ*) ont été comparées dans des conditions de terrain réelles. Les résultats ont démontré que le choix méthodologique influence les concentrations mesurées et la diversité des polymères identifiés. Bien que les deux approches présentent des tendances similaires au fil des campagnes et des gammes de tailles comparables, elles diffèrent dans la composition polymérique observée.

Ces résultats soulignent la nécessité d'harmoniser les méthodes de prélèvement sur le terrain et de garantir une transparence accrue dans la documentation des protocoles, afin d'améliorer la comparabilité des données entre études. Dans l'ensemble, les travaux mettent en évidence la complexité du devenir des microplastiques au sein des systèmes fluviaux urbains dynamiques et apportent des connaissances nouvelles permettant d'orienter et d'optimiser les stratégies futures de suivi, de modélisation et de gestion environnementale.

Mots clés :

Microplastiques, Seine, pollution urbaine, suivi de terrain, bilan massique

RÉSUMÉ SUBSTANTIEL DE LA THÈSE

IMPACT OF GREATER PARIS MEGACITY ON THE ABUNDANCE AND FATE OF SMALL MICROPLASTICS IN THE SEINE RIVER

Cette thèse vise à mieux comprendre l'abondance, la dynamique et le devenir des microplastiques dans les rivières urbaines, à travers l'exemple de la Seine dans la région parisienne. Les microplastiques, particules de taille inférieure à 5 millimètres, représentent aujourd'hui une source majeure de contamination des milieux aquatiques. Leur omniprésence, leur diversité morphologique et chimique, ainsi que leur persistance en font des polluants complexes dont les sources, les voies de transfert et les impacts restent encore imparfaitement caractérisés. Dans ce contexte, la Seine, soumise à de fortes pressions anthropiques, constitue un site d'étude particulièrement pertinent pour étudier la contamination en microplastiques dans un environnement urbain dense.

Les objectifs de ce travail sont triples : d'abord, quantifier les microplastiques présents dans la Seine et caractériser leur distribution spatiale et temporelle (avec un focus sur l'agglomération parisienne); ensuite, identifier les principales sources et voies d'entrée des particules dans le fleuve et estimer leur contribution relative à la charge totale ; enfin, évaluer les processus de transport, de rétention et de remobilisation des particules dans le continuum fluvial. L'ensemble du travail repose sur un suivi, réalisé entre 2021 et 2022, couvrant plusieurs stations situées en amont, au sein et en aval de l'agglomération parisienne.

Sur le plan méthodologique, la thèse a mobilisé des techniques de prélèvement et d'analyse à haute résolution. Les échantillons d'eau ont été collectés à l'aide d'un système de pompage et de filtration in situ en cascade (300 µm et 10 µm) sur quatre campagnes saisonnières sur l'ensemble des sites. Par ailleurs, un site (Bougival, Aval de Paris) a été sélectionné pour des campagnes avec des pièges à sédiments, permettant de comparer cette approche avec l'approche plus traditionnelle de pompage. Les particules collectées ont ensuite été isolées de la fraction minérale via séparation densimétrique. La fraction organique naturelle a par la suite été éliminée par traitement chimique. Les particules récupérées en fin de traitement (incluant les microplastiques) ont été, analysées par Imaging automatisé via spectroscopie infrarouge (µ-FTIR). La nature des polymères et leur morphologie a ainsi été identifiée. Des paramètres environnementaux tels que le débit de la rivière, les précipitations, la température et les volumes de rejets urbains ont été également suivi au cours de la période d'étude. Cette approche a permis de relier les variations des concentrations en microplastiques à des facteurs hydrologiques et anthropiques, tout en évaluant l'incertitude liée aux choix méthodologiques.

Les résultats révèlent une forte variabilité spatio-temporelle des concentrations en microplastiques, avec des valeurs comprises entre quelques dizaines et près de 4 700 particules par mètre cube. Cette variabilité reflète l'influence conjointe de la dynamique hydrologique, des épisodes pluvieux et des rejets urbains. Les concentrations les plus élevées ont été observées à proximité de la zone dense de Paris, en aval immédiat des stations d'épuration et des déversoirs d'orage. L'analyse des polymères met en évidence la

prédominance du polyéthylène, du polypropylène, du polystyrène et du polyéthylène téréphtalate, en cohérence avec les polymères les plus utilisés ainsi que ce qui est retrouvé dans la littérature.

Un bilan massique réalisé à l'échelle du tronçon étudié montre une augmentation nette de la charge en microplastiques entre l'amont et l'agglomération parisienne, traduisant un effet urbain marqué. Ce flux augmente de l'amont à l'aval. Toutefois dans les zones aval, proches de l'estuaire de la Seine, des diminutions sont observées et pourraient être attribuées à une baisse des concentrations dans la zone de dépôt de la rivière. Les crues et fortes précipitations entraînent une remobilisation partielle des particules piégées, provoquant des pics de flux en aval. Ces observations indiquent que la Seine agit à la fois comme vecteur de transfert et comme réservoir temporaire de microplastiques, avec des échanges dynamiques entre la colonne d'eau, les sédiments et les berges.

L'analyse comparative des méthodes de prélèvement constitue un autre apport majeur du travail. Les échantillons obtenus par pompage in situ t capturent une plus grande diversité de tailles de particules, tandis que les trappes à sédiments permettent d'échantillonner des polymères plus denses mais restent sensibles aux variations hydrodynamiques. Si les deux approches montrent des tendances similaires en termes d'abondance globale, elles diffèrent quant à la diversité polymérique détectée. Cette comparaison met en évidence la nécessité de standardiser les protocoles de prélèvement et d'analyse afin d'assurer la comparabilité des données entre études et de renforcer la fiabilité des bilans à l'échelle des bassins versants.

Les données suggèrent que les principales sources de microplastiques dans la Seine sont les effluents des stations d'épuration et les déversoirs d'orage, qui libèrent des flux importants lors des épisodes pluvieux. Les eaux de ruissellement urbain, chargées en microplastiques, contribuent également à la charge fluviale. Ces apports ponctuels et diffus sont dilués ou concentrés selon la morphologie du cours d'eau, la topographie des berges et la variabilité saisonnière du débit, produisant une distribution complexe des concentrations. La combinaison de ces facteurs rend difficile la prédiction directe du devenir des microplastiques sans modélisation intégrée. Néanmoins, les résultats de cette thèse apportent des éléments empiriques essentiels à la calibration de futurs modèles de transport et de rétention dans les milieux fluviaux.

Le manuscrit met également en lumière la complexité du comportement des microplastiques dans un système dynamique tel que la Seine. Les processus d'advection, de sédimentation, de remobilisation et d'agrégation interagissent selon les propriétés physiques des particules (taille, densité, forme) et les conditions hydrologiques.

Au-delà de la caractérisation des flux, cette recherche souligne les défis méthodologiques propres à l'étude des microplastiques en rivière. Les différences entre les approches analytiques, la variabilité naturelle du milieu et les incertitudes associées aux unités de mesure rendent les comparaisons inter-études délicates. Le travail recommande donc l'adoption de stratégies de suivi harmonisées, combinant un maillage spatial adapté et une fréquence temporelle suffisante pour capturer les variations hydrologiques. L'intégration des microplastiques dans les réseaux de surveillance existants permettrait de mieux documenter leur dynamique et d'améliorer les modèles prédictifs à l'échelle européenne.

Sur le plan environnemental, les conclusions de cette thèse rappellent que la pollution microplastique dans les rivières urbaines n'est pas un phénomène isolé mais d'une problématique bien plus large qu'est la consommation de plastiques. Les rivières concentrent les rejets issus des activités humaines et servent de vecteurs vers les milieux marins. Dans le cas de la Seine, les flux mesurés indiquent un transfert annuel de plusieurs tonnes de microplastiques vers l'estuaire, confirmant le rôle majeur des grands fleuves dans la dispersion mondiale de ces polluants. Les résultats invitent à repenser la gestion des rejets urbains, notamment par la réduction des apports à la source, l'amélioration du traitement des eaux usées et la maîtrise des déversoirs d'orage.

En fournissant des données quantitatives robustes, cette thèse contribue à combler les lacunes existantes sur la variabilité temporelle des microplastiques et sur leurs mécanismes de transfert en milieu fluvial. Elle met également en évidence la nécessité de tenir compte de plusieurs paramètres comme le débit, les rejets et les conditions météorologiques pour appréhender la complexité de la contamination plastique.

Enfin, cette recherche ouvre plusieurs perspectives. Elle appelle à la création de réseaux de surveillance transnationaux dédiés aux microplastiques, à l'intégration de ces données dans les modèles de gestion de la qualité de l'eau et à l'évaluation des risques écologiques associés. Elle encourage également l'harmonisation des protocoles à l'échelle internationale, condition essentielle pour établir des comparaisons fiables entre bassins versants. À terme, une meilleure compréhension du devenir des microplastiques en rivière permettra de concevoir des stratégies de réduction ciblées et de limiter leur transfert vers les océans. Les connaissances acquises sur la Seine constituent ainsi une base précieuse pour orienter la recherche, la surveillance et les politiques publiques en matière de pollution plastique.

ABBREVIATIONS AND TERMS

Abbreviation or term	Explanation
Advection	Particle transport with the water flow
CSO	Combined sewer overflow
Floodplain accretion	Depositions and accumulation of sediments along a river floodplain during flood events
FTIR	Fourier-Transform Infrared Spectroscopy, a method to identify microplastics and polymer types
Mobilization of MPs	MPs from within the riverine environmental compartment becoming available and getting suspended in the water column, e.g., resuspension from sediments
Morphological processes	Large scale processes affecting riverbed and shore, like erosion or displacement of sediments, e.g., dredging; can influence MP fate by burying or mobilizing particles
MP(s)	Microplastic(s)
P	Pump sampling with in-situ filtration, refers to chapter 5
Redistribution	Overall term for the three-dimensional (vertical and horizontal) movement of MP particle
Resuspension	Particle mobilization from the riverbed to the water column
Retention of MPs	MP accumulating in a place, temporarily or permanently held within a part of the river system; prevented from being transported downstream
River discharge/ river flow	Volume of water flowing through a river per time, measured in $m^3\ s^{-1}$
SSC	Suspended Solids Concentration, total insoluble particulate material in water
ST	Sediment Trap sampling, refers to chapter 5
Urban discharges	Includes sanitary and stormwater infrastructure; in this study we refer mostly to WWTP effluent and CSO discharge
WWTP	Wastewater Treatment Plant

CHAPTER 1 INTRODUCTION

This chapter provides the reader with an overview of microplastic pollution in rivers in urban areas and explains related research challenges.

1.1 BACKGROUND AND MOTIVATION

Throughout the earth's history **rivers** have been key to the survival and evolution of species including humans. With a global volume of ~2.000 km^3 rivers represent 0.006% of global freshwater resources. Hereby, rivers provide important ecosystem services like habitat refuge, water supply, climate regulation, nutrient cycling and transport (Schmutz & Sendzimir, 2018; Wetzel, 2001). Human settlements were often created near rivers, but urbanization altered the riverine landscapes (Wiens, 2002). With the acceleration of industry, technology and global trade, the load of pollutants in our environment increased over the past century (Meadows et al., 1972; Richardson et al., 2023). Today, river ecosystems are threatened by multiple pressures, like canalization, damming, water abstraction and pollutants, including novel entities like **microplastics (MPs)** (Schmutz & Sendzimir, 2018). MPs are plastic pieces smaller than 5 mm (NOAA, 2018; Thompson, 2004). The concept of the planetary boundaries (Rockström et al., 2009) considers MPs as emerging contaminants of concern (Richardson et al., 2023). MP are either formed through the breakdown of larger plastic particles or produced in small sizes. Several million tons of MP are released into our environment every year (OECD, 2022a). The sources for MP pollution are manifold: from broken plastic bottles to pre-production pellets or fibers shedding from clothing (OECD, 2022a; Thompson et al., 2024). While plastic can be a very useful material, its production includes the use of chemicals of which over 4200 are known to be concerning due to their persistence, ability to accumulate in organisms, mobility and toxicity (Monclús et al., 2025; M. Wagner et al., 2024). Due to the extensive scale of plastic pollution (OECD, 2022b) worldwide politics are discussing an international plastic treaty, but unfortunately no agreement has been formed yet.

Until around 2010, MP research focused mostly on marine ecosystems but has meanwhile extended to freshwater environments including rivers (Thompson et al., 2024). MPs in rivers can have negative effects on a wide variety of aquatic organisms, enter the food chain, accumulate, and are being transported to the marine environment. Research gaps regarding MPs in aquatic environments include fragmentation rates under different conditions, MP sources, quantities and transport in rivers, or long-term toxicological effects on biota. The international agenda seeks to improve water quality in surface waters with special attention to pollutants of emerging concern and their sources (OECD, 2016). After twenty years of research many scientific studies have proven the global omnipresence of MPs, but many matters remain to be understood (Thompson et al., 2024). With the continuous production and use of plastics, MPs will accumulate in our environments (OECD, 2022b), further fragment to nanoplastics (smaller than 1 µm), and the problems will likely increase and/or new problems may arise (Niu et al., 2024; Thompson et al., 2024). Thus, to fill the knowledge gaps, more and better data is needed. With the help of field measurements we can quantify MPs in rivers, assess the level of pollution, and gain

further insights into MP sources, entry pathways, fate and transport (Koelmans et al., 2019). Monitoring approaches with larger temporal and spatial coverage and higher data resolution should receive special consideration. Different to one-time samplings that provide only a snapshot of MPs pollution, monitoring approaches help to understand temporal and spatial patterns, which ultimately are linked to MP release from sources and environmental fluctuations (Kukkola et al., 2024; United Nations Environment Programme, 2020). With the evolution of improved sampling and analytical methods for MP research such monitoring studies have become more feasible. The results of such studies are useful to identify MP sources and inform environmental management to continue to protect river ecosystems. The city of Paris and other urban metropolitan areas in the world are hotspots of MP sources and their rivers are key receiving environments, making them important monitoring areas.

1.2 MICROPLASTICS: MULTIFACETED CONTAMINANTS

1.2.1 DEFINITION AND TERMS

1.2.1.1 Plastic production, types, and chemicals

Plastic production belongs to the petrochemical industry as over 90% of plastics are fossil fuel based (Kutz, 2016; Plastics Europe, 2025). Since the 1950s, annual global plastic production has increased exponentially to reach 430 million tons in 2024, with Europe accounting for around ~12%[1] (54 million tons) and generating an economic turnover of around 400 billion € (Plastics Europe, 2025). Over nine billion tons of plastic have ever been produced (Figure 1–1). The annual per capita plastic waste ranges from 14 kg (India) over 122 kg (EU countries) to 220 kg (USA) (OECD, 2022a). Of the plastic produced, some remains in use (stock), some is incinerated, a small portion is mechanically recycled, most is discarded, and part leaks into the environment (Geyer et al., 2017).

[1] Statista, 26.10.2025

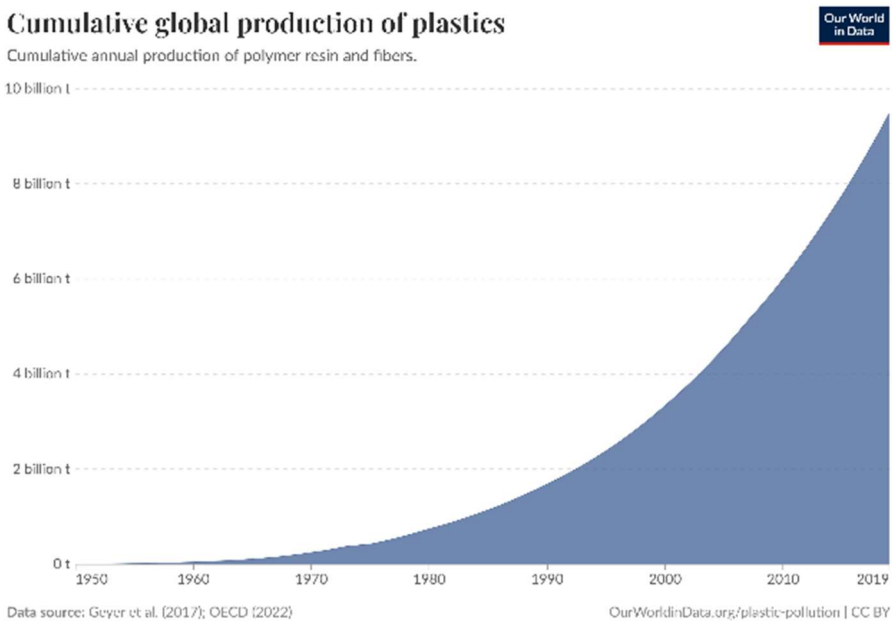

Figure 1–1 *Global cumulative plastic production. Graph: Our World in Data, 2025.*

Mismanaged waste, around half of all waste (The PEW Charitable Trust, 2020), is the most important reason of plastic leakage to the environment (82%), while the remaining parts are estimated to come from marine activities (1%), transport related (MPs) (for definition see section 1.2.1.2) (4%), MP dust (3%), wastewater sludge (3%) and other sources (OECD, 2022a). In 2019, about 22 million tons of plastic leaked into the environment based on estimations of the OECD. Plastic also contributes to global greenhouse gas emission (~4%) and the industry contributes to habitat destruction, for example for building production plants for chemicals used in the making of plastics (Correia, Mickaël, 2022; Rucevska et al., 2024). With projections for recycled plastic percentage in plastic stock from about 7% today to only 12% in 2060, a continued increase in plastic production is definite (OECD, 2022b). With that, plastic leakage to the environment is to double by 2060 (to 44 million tons per year).

Plastic is a group of materials with different types used for a huge array of applications, from packaging to fishing gear, clothing, high-tech applications, paint, construction, or ingredients in personal care products (GESAMP, 2015; Kazemi et al., 2021). Plastics are synthetic polymers and consist of chains of macromolecules (such as ethylene [$H_2C{=}CH_2$] forming polyethylene [$H_2C{=}CH_2]_n$) that underwent polymerization. Two types of plastics are distinguished based on their molecular chain structure: thermoplastics and thermosets (Table 1–1). Thermoplastics can be melted when heated and hardened when cooled, while thermosets undergo a chemical change when produced and re-melting or re-forming is not possible (Kutz, 2016). Plastic can have different physical properties and be rigid or more flexible, such as rubbers.

Table 1–1 *Common classification of plastics by production process and physical properties with some examples. Table modified from (Kutz, 2016).*

	Thermosets	**Thermoplastic**
Rigid	Phenol-formaldehyde resin (Bakelite) Epoxy Phenolic Acrylic or polymethyl-methacrylate (PMMA)	Polystyrene (PS) Polypropylene (PP) Polyvinyl chloride (PVC) High-density Polyethylene (HDPE) Polycarbonate (PC)
Flexible	Vulcanized rubbers	Low-density polyethylene (LDPE) Plasticized Polyvinyl chloride (PVC)
Rubbery	Vulcanized rubbers, like natural rubber (NR) or styrene-butadiene rubber (SBR)	Thermoplastic elastomers

The most used polymers are of the thermoplastic material type. Some of the most well-known plastics are polyethylene (PE, percentage of global plastics production ~26%), polypropylene (PP, ~19%), polyvinyl chloride (PVC, ~13%), polyesters to which also polyethylene-terephthalate (PET, ~6%) belongs, polystyrene (PS, ~5%), polyurethane (PU or PUR, ~5%) (Plastics Europe, 2025). Some polymer types are mostly used for the production of textiles and produced as fibers, like polyesters, polyamides (PA) and acrylics (Geyer et al., 2017). Other polymers are usually used in plastic pellets for the making of all kinds of plastic items, like automotive parts, or as powder and used in paints or coatings or other high-tech applications (Geyer et al., 2017; Kutz, 2016). PP is commonly used for medical or food contact products, PE for packaging and often plastic bags, and PS for applications like insulation, food packaging and PVC is dominant (~69%) in the construction sector (Geyer et al., 2017; Plastics Europe, 2019).

Depending on the plastic type and application different chemicals (on average 7% of the mass) (Geyer et al., 2017) are used in their production. While processing parameters like temperature, pressure and catalyst substances are used to control the polymerization process when making plastics from monomers, the addition of other substances (chemicals) are important for shaping plastic properties like heat resistance or flexibility (Kutz, 2016; M. Wagner et al., 2024). There is a multitude of additives like plasticizers, stabilizers, flame retardants, modifiers, antioxidants, pigments, biocides, and even fragrances, many of which are known to be harmful or toxic (Kutz, 2016; Monclús et al., 2025; M. Wagner et al., 2024). Recent studies identified the mixture of chemicals used in plastics and found over 16,325 chemicals and discovered a concerning amount of non-intentionally added substances that can form during processing (M. Wagner et al., 2024). Due to the diversity of the plastic processing industry and a systematic lack in the regulation and control of chemicals, information for various chemicals is unknown. With scientific proof of the release of chemicals from plastics by migration or volatilization, there is growing concern about the toxicity and health effects on humans and in the environment (Monclús et al., 2025; Stevens et al., 2024; M. Wagner et al., 2024).

1.2.1.2 Microplastics

Plastics between 1 and 5,000 µm (5 mm) are microplastics (MPs). Sometimes, MPs of 1 – 5 mm size are called larger MPs (International Organization for Standardization, 2023; Thompson, 2004). Below 1 µm, plastics are referred to as nanoplastics (also: NPs) (Figure 1–2) (European Commission, 2023). All MPs originate either from the intentional production of small plastic particles (primary MPs) or from the fragmentation of larger plastics induced by physical, biological, and chemical impacts (secondary MPs) (Browne, 2007; Thompson, 2004). Examples of primary MPs are pre-production pellets or micro beads for application in industry. Examples for secondary MPs are small fibers from synthetic clothing, fragments from car tires, or pieces broken off from any kind of plastic product. Due to the way MPs are formed, they can be of all kinds of shapes, which are often categorized as fibers, spheres, fragments and films (Hartmann et al., 2019; Kooi & Koelmans, 2019). However, other descriptions proving more detail depending on the context of studies are used, such as foams. While soluble plastics exist, most plastics are particulate and insoluble, and this thesis further refers to the latter. Figure 1–3 shows an example of a yellow MP fragment found in the Seine River.

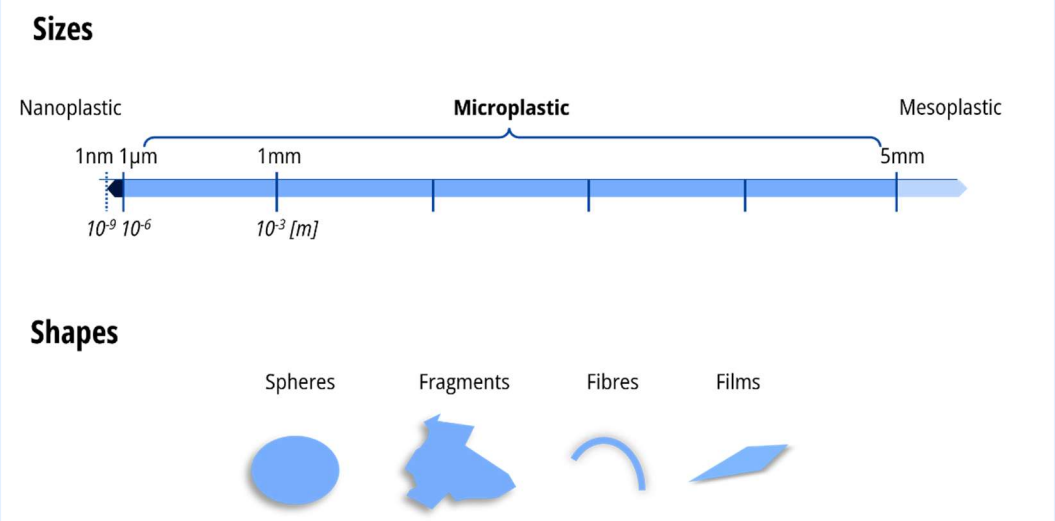

Figure 1–2 *Plastic size categories and basic shape categories for microplastics*

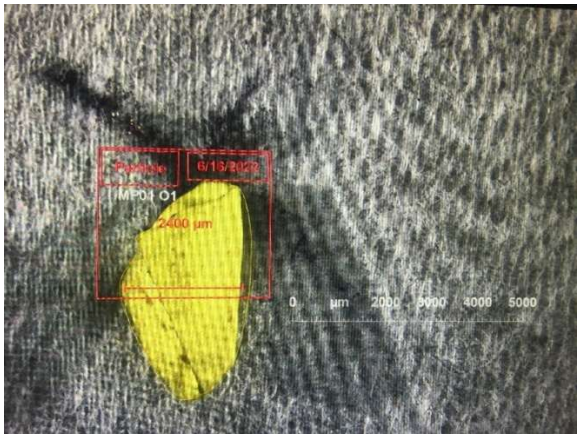

Figure 1–3 *A yellow microplastic (MP) particle under the microscope from this study. Scale in µm. Own photo.*

All MPs have two common inherent characteristics: they are made of polymers through a polymerization process (see 1.2.1.1), and the particles are smaller than 5 mm (and optionally above 1 µm). Otherwise, MPs are diverse. Specific features are the plastic type, shape, chemical composition (polymer and other additives), color, or origin/source (Rochman et al., 2019). Table 1–2 summarizes key features of MPs and the environmental relevance in freshwater. Because of the different types and properties, MP are considered a diverse group of contaminants (Rochman et al., 2019; Thompson et al., 2024).

MPs are persistent in the environment due to their chemical and physical properties, but this differs depending on the mix of features for each piece of MP. Typical for MPs are their chemical-physical persistence in the environment lasting potentially up to hundreds of years (Chamas et al., 2020; Sutkar et al., 2023). However, MPs are subject to fragmentation (break-up) and degradation (reduction of the molecular mass) over time, together also referred to as weathering (Andrady & Koongolla, 2022). Physical, chemical and biological mechanisms influence weathering (Chamas et al., 2020). Abrasion and contact with other hard materials, like sand in river sediments, can cause diffraction of the plastic particle surface and accelerate breakup. The result is a gradual breakdown of MPs into smaller particles, eventually leading to the formation of nanoplastics (Pfohl et al., 2022). With a decrease in particle size the surface-area-to-volume ratio increases. Degradation reduces the molecular mass of the plastic particle through five processes: photolysis, thermal degradation, oxidation, hydrolysis, or biological activity (Andrady & Koongolla, 2022). Degradation processes lead to the release of chemicals and affect the surrounding environment. UV radiation, for example, weakens the molecular bonds of the plastic material and leads to further breakdown, break up, and release of chemicals (Pfohl et al., 2022). The fate of MP particles in the environment depends on multiple factors, such as the type of plastic (main density property), size, shape, or biofilm attachment (see also section 1.3.3). Biofilm on the surface, leaching chemicals, or adhesion of external chemicals can change the density of the MP particle (Andrady & Koongolla, 2022). The intensity and duration of exposure to different degradation and fragmentation further influence the MP particle fate.

1.2.2 ENVIRONMENTAL SIGNIFICANCE OF MICOPLASTICS (MPs)

Microplastics (MPs) pollute the soil, air and water, causing problems for ecosystems (Jambeck et al., 2015a; Lau et al., 2020; Schmidt et al., 2017). The environmental consequences of MP pollution are not fully understood (Thompson et al., 2024; M. Wagner & Lambert, 2018, p. 196; Windsor et al., 2019), but a growing body of scientific evidence shows that MP can have severe impacts on organisms with repercussions across the food web (Cole et al., 2011; Mao et al., 2022; Monclús et al., 2022) including effects on humans (Emenike et al., 2023; Nihart et al., 2025; M. Wagner & Lambert, 2018, p. 189; Yan et al., 2021; Yu et al., 2024) and ecosystems functioning (Green et al., 2017; Rillig et al., 2021). Because of the small size, MP particles can spread widely and easily be ingested/taken up by small organisms (Cole et al., 2011; Koelmans, 2015). In addition, the chemical composition and potential to leach chemicals adds another layer of risk (see also 1.2.1.1). A recent study by Stevens et al. (2024) found chemicals in different food-contact plastics including the common plastics PE, PET, PP, PS, PU and PVC. Their study showed that

most tested plastics released chemicals that can affect human health, for example through endocrine disrupting mechanisms. They further highlighted a vast number of chemical features present in the different plastic types and proved that those chemicals are impacting.

In the Water Framework Directive (European Commission, 2000), pollution is defined as "*(…) the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems (…).*". This includes "*Substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment.*". The directive further explains 'hazardous substances' to which, considering the current state of the science (Monclús et al., 2025; M. Wagner et al., 2024), MPs belong.

Numerous research studies have shown that freshwater ecosystems and organisms are negatively impacted by MPs (D'Avignon et al., 2022). For example, freshwater amphipods grind and fragment plastic type Acrylonitrile Butadiene Styrene (ABS), which raised their stress levels (Queiroz et al., 2025). The similar effect has been observed with algal growth (Queiroz et al., 2025; Senturk, 2024). PVC induced toxic effects on freshwater biota, not necessarily from leachate but other material-chemical-related characteristics of MP particles (Scherer, Wolf, et al., 2020). Ecotoxicological effects of PET were reported on the growth of and photosynthetic activities of algae (Pencik et al., 2023). Other studies showed effects on the clearance rate of freshwater bivalves due to exposure to PS (Weber et al., 2021). However, laboratory-based toxicity studies often use MP concentrations which exceed concentration found in the environment. An environmental risk assessment was used to determine microplastic thresholds for ecotoxicological evaluation, with the results showing clear impacts on aquatic ecosystems (Rico et al., 2023). The evidence of the physical and chemical impacts of MPs on freshwater ecosystems, particularly on biota, is clear. As rivers are receiving and transitory environments for MP, it is important to understand the impact.

Table 1–2 *Microplastic properties and features that are relevant to MP fate and environmental risk in aquatic environments.*

Feature	Categories	Description
Size at production	<5mm	Microplastics are likely to be ingested by organisms and can penetrate small environments
	>5mm	Meso- or macroplastics, can fragment into microplastics
Shape		Shape is an important feature for bioavailability and particle fate, especially in waters.
	Sphere	Spheres or ellipsoids, often as primary MPs from personal care products (regulated since 2023, Commission Regulation (EU) 2023/2055 2023), or as pre-production pellets
	Fragment	Fragments all have different, often unidentifiable forms, commonly observed shape in the environment
	Fiber	Fibers defined as fibrosus particles with thickness to length ratio over 1:4, commonly observed shape in the environment
	Film	Films usually come from packaging and foils
	Foam	Foams are plastics which are expand with air, like expanded polystyrene (EPS)
Material type	Thermoset	Undergo irreversible chemical change when heated, no re-melting or re-forming possible afterwards
	Thermoplastic	can be melted when heated and hardened when cooled
Polymer type (common density range in g cm^{-3})	Acrylonitrile Butadiene Styrene: ABS (~1.12)	Polymer type is the base chemical fingerprint and usually refers to the main polymer a plastic piece is made of. Polymer types have unique wavelength spectra, a property that is used in polymer identification techniques such as FTIR. For more details see also Supplementary Information (SI) of chapter 4.
	Acrylic	
	Polyamide: PA (1.02 – 1.16)	
	Polyethylene: PE (0.89-0.98)	
	Polypropylene: PP (0.83 – 0.92)	
	Polystyrene: PS (1.04 – 1.1) / Expanded PS: EPS (0.02-0.06)	
	Polyurethane: PU (~1.23)	
	Poly vinyl chloride: PVC (1.1 – 1.58)	
	Styrene butadiene rubber: SBR (~0.94)	
Additives	Phenols	Additives are chemicals used to modify the properties of plastics, such as flexibility, color, durability, and scent. These chemicals can leach out and contribute to chemical pollution, affecting aquatic organisms. The effects of additives can be assessed using hazard criteria.
	Phthalates/softeners	
	Flame retardants	
	Heat stabilizers	
	Lubricants	
	Dyes	
	Fragrances	
	Plasticizers	
	Other ingredients	

Density	ρ in g cm^{-3}	Plastic densities are determined by polymer type and additives, hence, the variety of density even for the same polymer type can be high. Density is an important feature for the MP fate in waters, MPs with a density below that of water (~1 g cm^{-3}) are likely to float and with a higher density are likely to sink.
Hazard criteria	Persistence Bio-accumulative Mobile Toxic	Known as PBMT hazard criteria. The criteria refer to four important properties that determine their time to remain in the environment (persistence), tendency to accumulate in organisms (bioaccumulation), ability to move across environments and compartments (mobile), and their potential to harm organisms.
Type of release to the environment	Intentionally Unintentionally	Intentional release examples are microbeads from personal care products (now mostly regulated) Unintentional release is, for example, tire wear abrasion, textiles wear and tear

1.3 MICROPLASTIC POLLUTION IN URBAN RIVER CATCHMENTS: RESEARCH AND KNOWLEDGE GAPS

Concentrated anthropogenic activity is one of the main mechanisms causing increased plastic and MP waste (L. Lebreton & Andrady, 2019) and release to the environment (Hitchcock & Mitrovic, 2019; Kunz et al., 2023). This is especially true for rivers in urban areas, with densely populated areas and peak human activities (Fang & Jawitz, 2019). Commonly, MPs enter rivers from land through littering, surface runoff or flooding, through activities in the ecosystems, such as boating, or via urban infrastructures like combined sewer overflows (CSOs) or wastewater treatment plants (WWTP) effluents (Dris et al., 2016; Fahrenfeld et al., 2019; Mao et al., 2022).

1.3.1 HOW POLLUTED ARE URBAN RIVERS?

Riverine freshwaters near urban agglomerations are especially subject to microplastic (MP) contamination (Lechner et al., 2014; Skalska et al., 2020). The scale of the MP pollution hereby is strongly determined by MP sources in the area (see 1.3.2), the downstream transport of MPs along the river, and the MP fate within the river (see 1.3.3), for example particle movements. Over the past decade, there has been a huge increase in the number of studies. A SCOPUS search using the keywords 'Microplastic' and 'River' returned 3,225 documents from 2013 to the present day, with most articles (47%) regarding Environmental Sciences. This significant advancement in science has resulted in initial estimates and insights into MP abundance and its fate in various rivers worldwide (D'Avignon et al., 2022; Scherer, Weber, et al., 2020; Tan et al., 2023). Generally, reported MP concentrations were relatively similar in rivers compared to marine environments (Waldschläger, Lechthaler, et al., 2020). Rivers also play a key role in the transitional transport of MPs between terrestrial ecosystems and to the marine environment (Buschman et al., 2020; L. C. M. Lebreton et al., 2017; Schmidt et al., 2017; Wu et al., 2020). MPs have been identified in rivers all over the globe and studies assessed MP in river water, sediment and in organisms (Li et al., 2020; Tan et al., 2023). Globally, MP concentrations of up to 10^6 pieces m^{-3} have been found, with large variations and smaller particles being more abundant (Scherer, Weber, et al., 2020; Tan et al., 2023). MP concentrations found in European rivers range from less than one to 3.45 x 10^5 particles m^{-3} with significant variations (Scherer, Weber, et al., 2020).

1.3.1.1 MP abundance

Figure 1–4 and Table 1–4 present a selection of MP abundance data from European rivers and many related to urban catchments, including reported minimum and maximum values, means and medians, and MP size limitations. The data includes studies that sampled MP in the water column or river sediments. Some studies report lower MP concentrations, such as in the Elbe River (Germany) or the Gave de Pau River (France), where concentrations in the river surface were just a few particles m^{-3} (Bruge et al., 2020; Scherer, Weber, et al., 2020). Larger Rivers, like the Rhine (Germany) exhibited similarly low

concentration in one study (Erni-Cassola et al., 2024), but extremely high concentrations were reported in another study in the Dutch Rhine (Leslie et al., 2017). The Rhône (France) was reported to have a mean of 11 particles m^{-3} (Constant et al., 2020). For the Seine River (France) MP abundance was reported ranging from 0.3 to 15,000 particles m^{-3} (Dris, Gasperi, et al., 2015; Treilles et al., 2022). The London Thames, a highly polluted river in the urban vicinity had also high MP concentrations with a mean of 12,000 particles m^{-3} (Devereux et al., 2023). In the sediment of rivers, studies often report MP abundance in the 10^2 – 10^7 magnitude (D'Avignon et al., 2022; Scherer, Weber, et al., 2020). River sediments contain a lot of MP and are often regarded as MP sinks (Nizzetto et al., 2016), hence comparison or consideration of other river compartments is therefore important.

There is obviously a large variation in MP abundance across the studies and sometimes also within one study or one river. However, more similar patterns are seen for MP size distributions, shapes, and dominant polymer types. While studies find varying shapes, most common are fragments and fibers, with dependencies on the sampling method. Most studies report more particles in smaller size classes. This is a phenomenon possibly linked to MP fragmentation. In line with the global production of plastics, which is estimated to increase further in the future (L. Lebreton & Andrady, 2019), the most frequently found polymer types in aquatic environments are PE, PP, PS, PVC, and PET (Koelmans et al., 2019; Li et al., 2020; Tan et al., 2023). Also, acrylic and polyester are often reported. Within a river, MP abundances vary between sediments and water. In the Elbe River, for example, smaller particles and a higher number of different polymer types were found in sediments than in the water (Scherer, Weber, et al., 2020). MPs with higher density, like PVC or acrylics, are often better retained in sediment (Nizzetto et al., 2016) but can be resuspended into the water columns.

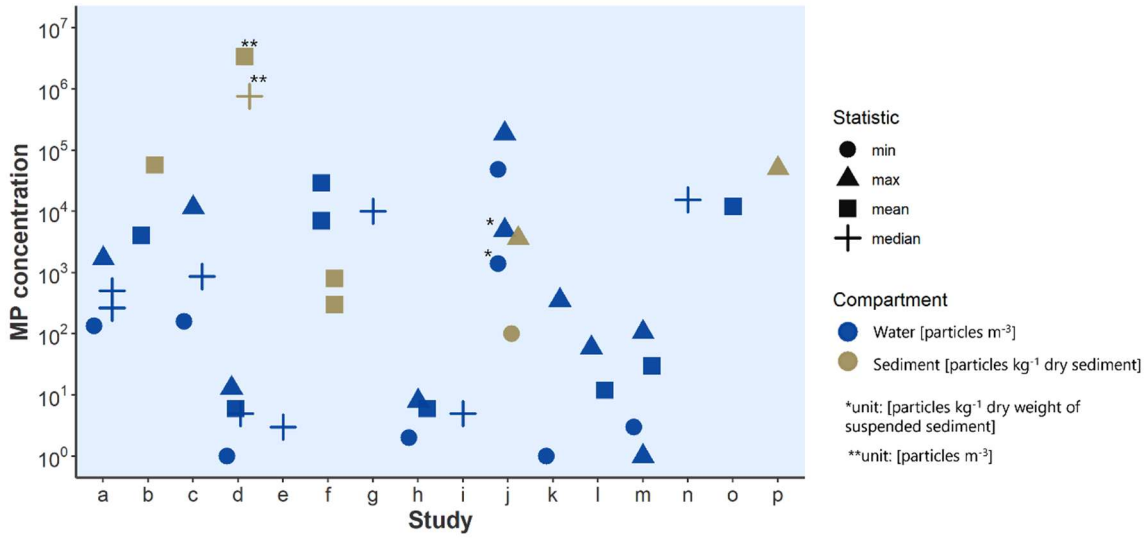

Figure 1–4 *Microplastic (MP) concentrations of different studies in European rivers in river water (blue) and sediment (brown). Logarithmic y-axis. Studies a – p are referenced and described in Table 1–4. a: Amsterdam canals (NL), b: Besòs and Tordera basin (ES), c: Dommel (NL), d: Elbe (DE), e: Gave de Pau River (FR), f: Loire (FR), g: Parthe (DE), h: Po (IT), i: Rhine (DE), j: Rhine (NL), k: Rhine and Danube catchment (A), l: Rhône (FR), m: Seine (FR), n: Seine (FR), o: Thames (UK), p: Seine (FR)*

Studies showed different spatiotemporal patterns of MP levels in urban rivers. Spatial analyses typically examine how MP concentrations vary across various locations along the river or catchment or, on a smaller scale, in a river cross section. Some studies have linked higher MP concentrations to urban sources such as WWTP effluent outlets and CSOs. (Leslie et al., 2017; Nguyen et al., 2024; Schmidt et al., 2020). Other studies observe MP increasing along with the urban gradient and suspect population density or human activity are influencing factors (Gonzalez-Saldias et al., 2024; Sefiloglu et al., 2024). Other studies could not find any clear or significant patterns and just reported general fluctuation of MP levels or observed general spatial trends (Vidal et al., 2023).

Studies analyzing temporal patterns usually consider yearly seasons (like summer or winter) or understanding the hydrological regime (the characteristic pattern of water flow over time), related to meteorological conditions. While some studies observe seasonal fluctuations, of which some could be related to the river flow regime, many studies did not detect obvious temporal trends (Mintenig et al., 2020). Two studies in France observed higher MPs during floods in the Seine and Rhône River (Constant et al., 2020; Treilles et al., 2022). However, temporal and spatial effects might interact, for example, a local CSO can lead to higher MP levels during rain events (Constant et al., 2020). There are not many studies yet that investigate overlaying spatiotemporal effects.

1.3.1.2 Challenges

In fact, many studies investigate a limited number of sampling sites in a small section of a river over a short period of time, a method known as snapshot sampling. The limited temporal and spatial resolution of the data make it difficult to draw reliable conclusions. More frequent measurements are needed to create a more accurate picture of the MP level in a river (D'Avignon et al., 2022; Kukkola et al., 2024). Due to the large scale of many river catchments, difficulty accessing certain locations for sampling, and the diversity of MP sources along a river, comprehensive studies (Constant et al., 2020; Dris, Gasperi, & Tassin, 2018; Gonzalez-Saldias et al., 2024; Leslie et al., 2017; Schrank et al., 2022) are still rare, often due to the lack of feasibility and resources. In addition, the combination of MP data with environmental parameters (e.g., precipitation or potential sources) is often not considered, and limited datasets hamper comprehensive analyses. However, comparisons between studies help to gain insights into possible MP dynamics in urban rivers and form hypotheses (Schrank et al., 2022; Skalska et al., 2020).

The variations across results of different studies suggest that MP concentrations are not consistent throughout European rivers (D'Avignon et al., 2022; Dris, Imhof, et al., 2015). Part of the observed variations can be true temporal and/or spatial heterogeneity due to MP dispersion throughout the water column, MP release from sources, or MP mobilization, influenced by river hydrodynamics. This variation also hampers statistical analysis and while trends can be observed there might be no statistical significance. The studied rivers differ in sizes, morphology, and hydrodynamic conditions and are often situated in very different geographic regions, a fact that makes comparisons of reported MP levels more difficult (Schrank et al., 2022). In addition, the comparability between studies is hampered due to the different sampling and analytical methods used (see also 1.3.4). Therefore, comparisons and evaluations of the level of MP pollution should be made with caution and cannot be taken as absolute pollution levels.

While researchers commonly report MP concentrations, they rarely quantify the MP load or flux, which is another way of measuring MP pollution in rivers.

$$MP\ load\ =\ MP\ concentration\ \times River\ flow \quad \text{(Equation 1.3.1.2–1)}$$

When calculating the MP load of an entire river, the underlying assumption is that the MPs are homogeneously distributed in the water, which is not the case (Waldschläger, Lechthaler, et al., 2020). Load estimates can give insight into the potential overall MP load in a river, help create mass budgets, and establish links between MP abundance and river size/flow conditions, so in understanding transport dynamics (see section 1.3.3).

Another reason for challenges in comparing MPs across environmental sections is the unit of measurement (Dris, Imhof, et al., 2015; Scherer, Weber, et al., 2020). Studies report range and mean or median concentrations, but the data reporting is not consistent across studies (see Table 1–4). The measurement of MPs is often based on a volume of liquid (particles per liter or m^3), rather than per mass of (total) suspended solids (TSS) (particles per gram of TSS in the water). Some studies approach this and report MP per suspended solids in the water (Leslie et al., 2017), but if not done across research consistently, comparisons are not possible. MP numbers per liquid volume may not be the most appropriate way to measure MPs, as they are a particulate pollutant. In river sediments, MPs are often reported as a number per sediment mass, but it is unclear how this would translate into actual MP numbers per volume of water. However, it would be comparable with the measurement per suspended solids. Table 1–3 below summarizes common pitfalls that hinder cross-study comparisons.

Table 1–3 *Summary of comparability problems across field studies and MP data reported in freshwater environments.*

What hinders comparability across studies?
– No harmonized/standardized methods or monitoring strategies/approaches
– Differences in targeted MPs (e.g., size, type)
– Limited number of studies
– Limited temporal and spatial resolution of the data
– Lack of data of other environmental parameters measured in parallel
– Different units of measurement
– Inconsistency in data reporting and transparency
– Lack of understanding of MP fate
– Natural variation of ecosystems

MP pollution and the dynamics in rivers are not yet comprehensively explored because of the complexity of the subject and the effort and resources required (Schrank et al., 2022; Skalska et al., 2020). Hence, long-term assessments and comparisons on a larger scale (e.g., Europe) are not yet implemented. Most studies are snapshots but it is suspected that such samplings are not enough (Kukkola et al., 2024) and regular monitoring is highly recommended (D'Avignon et al., 2022). The small amount of field data and lack of

comprehensive studies, as well as comparability between study results are important problems. Harmonized and standardized monitoring would help to gather more comparable data faster and advance on MP fate modeling, understanding of sources and impacts (D'Avignon et al., 2022; Thompson et al., 2024). MP pollution in rivers is proven within rivers globally, although with high variation in concentrations. Multiple studies identify MP hotspots or sinks, which could be especially relevant in terms of toxicity.

Table 1–4 *Levels of microplastic (MP) pollution in river water (blue) and sediment (brown) of different European rivers, sorted by River or catchment name alphabetically. Units for all concentrations for water were converted to particles (p) m^{-3}, unless indicated differently. Units for sediment concentration were given as particles (p) kg^{-1} dry sediment.*

	Study	River (Country)	MP information	MP sizes	Reference
Water	a	Amsterdam canals (Netherlands)	Range: 134 – 1,707 Median summer: 508 Median winter: 263	25 – 300 µm	(Sefiloglu et al., 2024)
	b	Besos and Tordera basin (Spain)	Mean: 3,500 ± 3,300	>50 µm	(Gonzalez-Saldias et al., 2024)
	c	Dommel (Netherlands)	Range: 160 – 11,532 Median: 862	>20 µm	(Mintenig et al., 2020)
	d	Elbe (Germany)	Mean: 5.6 Median: 5.1 Range: 0.8 – 13.2	150 – 5,000 µm	(Scherer, Weber, et al., 2020)
	e	Gave de Pau River (France)	Range: 2.64 – 4.24 Median: 3.26	> 330 µm	(A. Bruge et al. 2020)
	f	Loire (France)	Means: 7,000 – 29,000	25 – 5,000 µm	(Vidal et al., 2023)
	g	Parthe (Germany)	Median: 10,000	500 – 1,000 µm	(S. Wagner et al., 2019)
	h	Po, Italy	Mean: 6 Range: 1.9 – 8.2	330 – 5,000 µm	(Fiore et al., 2022)
	i	Rhine (Germany)	Median: 4.48 Range MP load: 4×10^{2} – 3.6×10^{5} *[p s^{-1}]*	50 – 3,000 µm	(Erni-Cassola et al., 2024)
	j	Rhine (Netherlands)	Range: 48,000 – 187,000 Range: 1,400 – 4,900 *[kg^{-1} dry weight of suspended solids]*	10 – 5,000 µm	(Leslie et al., 2017)
	k	Rhine and Danube catchment	Range: 0.7 – 355	> 300 µm	(Schrank et al., 2022)
	l	Rhône (France)	Mean: 11.6 Range: 0.3 – 59	> 333 µm	(Constant et al., 2020)

			Mean annual MP load: 5.92 *[t yr^{-1}]* Mean annual MP load per catchment: 61 *[g km^{-1}]*		
	m	Seine (France)	Range : 3 – 106 Mean: 30	80 µm – 5,000 µm	(Dris, Gasperi, et al., 2015)
			Range: 0.3 - 0.5 Mean: 0.35	> 330 µm	
	n	Seine (France)	Median: 15,500 Range MP mass flux: 924 – 1,675 *[t yr^{-1}]*	> 80 µm	(Treilles et al., 2022)
	o	Thames, UK	Mean: 12,000 p m^{-3}	11 – 5,000 µm	(Devereux et al., 2023)
Sediment	b	Besos and Tordera basin (Spain)	Mean: 56,900 ± 39,900	< 0.032 mm – >2 mm	(Gonzalez-Saldias et al., 2024)
	d	Elbe (Germany)	Mean: 3.35 × 10^{6} *[p m^{-3}]* Median: 7.6 × 10^{5} *[p m^{-3}]*	125 – 5,000 µm	(Scherer, Weber, et al., 2020)
	f	Loire (France)	Mean upstream: 300 Mean downstream: 800	25 – 5,000 µm	(Vidal et al., 2023)
	j	Rhine (Netherlands)	Range: 100 – 3600	10 – 5,000 µm	(Leslie et al., 2017)
	p	Seine (France)	Max: ~50 × 10^{3}	25 – 500 µm	(Bouzid et al., 2025)

1.3.2 MP SOURCES AND ENTRY PATHWAYS

There are multiple ways of how MPs enter rivers from a variety of sources (McCormick et al., 2016; Thompson et al., 2024; Waldschläger, Lechthaler, et al., 2020). There is a distinct difference between what an MP source is and what the entry pathway to a receiving environment is. **Sources** can be defined as any product, object or process that releases MPs. The way MPs enters the receiving environment, for example a river, can be considered the MP **entry or release pathway** (Bergmann, 2015; Waldschläger, 2020). MP entry be categorized in diffuse (spread) and point (at a specific location) pathways that constantly or temporarily release MPs into rivers (Table 1–5). Besides, human activities and natural processes can facilitate the entry of MPs. For example, wind and rain could cause atmospheric redistribution and surface runoff, while human activity like traffic could also cause MP release to a nearby river.

1.3.2.1 Sources

Most sources of MP are land-based (Geyer et al., 2017; Jambeck et al., 2015b; The PEW Charitable Trust, 2020). Table 1–6 and Figure 1–5 provide an overview of common MP sources and their entry pathways to rivers. Fragmentation of larger plastics is estimated to be the largest source of MP with over 7,000 tons of leakage per year (Thompson et al., 2024). Paints (average MP content 37%) and tire abrasion are also major MP sources (Paruta et al., 2022; Thompson et al., 2024). Uncontrolled processes such as abrasion of paint coatings or wear and tear of larger plastic items are source of MPs (Jambeck et al., 2015a; The PEW Charitable Trust, 2020). Synthetic textiles shed MPs, also referred to as microfibers, which are commonly found in rivers (see section 1.3.1). Pre-production pellets are often released in large quantities via spills, such as during a spill in Western Spain in 2023 where 25 tons of nurdles were released to the sea (Vidal-Abad et al., 2024). Recently, artificial turf used in sport facilities has been identified as an MP source as well (Sundt et al., 2020). Moreover, personal care products are known to release MPs, especially via the household sewer system (Thompson et al., 2024). Agricultural plastic applications like mulching can also lead to MP release to the environment (Rehm et al., 2021). A very relevant issue is the application of WWTP sludge on fields, which accumulates around 99% of MP from wastewater on agricultural fields (Corradini et al., 2019; Zhang et al., 2020). MP from fields can enter rivers via erosion or runoff. There are also MP sources within the river related to its use, such as shipping, boating or fishing (Thompson et al., 2024).

1.3.2.2 MP release pathways

Precipitation in river catchments is an important influence on the river discharge in the catchment. Linked to higher water levels and increased river flow rates, erosion and/or submersion of riverbanks including floodplains can mobilize MPs from bank and overbank areas (Skalska et al., 2020). Urban areas with high human activities and an accumulation of MP sources release more MPs to rivers. The discharge from WWTPs and CSOs are some of the most important MP pathways to rivers and many studies have shown impact on river MP concentrations (Bollmann et al., 2019; Dyachenko et al., 2017; Thompson et al., 2024). Many activities and processes facilitate the release of MP in the close

surrounding of rivers, either on surfaces or in the air, entering rivers through atmospheric and wind-driven deposition, stormwater runoff during precipitation, littering, or other processes. Rainfall causes surface runoff, which leads to the entry of inorganic and organic matter from the surroundings, including MPs (Dramais et al., 2018; Ross et al., 2023). Strong rainfall leads to urban wastewater discharges and contributes to MP in rivers (Imbulana et al., 2024). MPs enter together with stormwater runoff, WWTP effluent discharge, and/or CSO discharge.

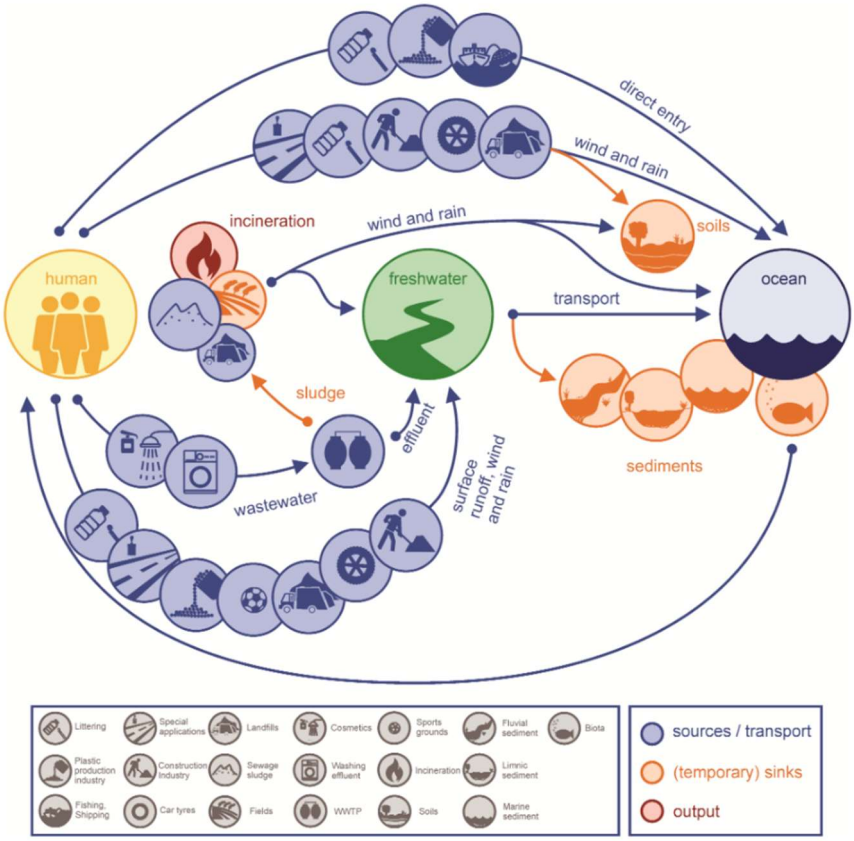

Figure 1–5 *From: Waldschläger, Lechtaler et al. (2020). The figure visualizes MP sources, pathways entering the environment and transport in the environment.*

Depending on the amount of sealed surface in urban areas and the type of sewer infrastructure, precipitation can lead to CSOs (Even et al., 2007; Tabuchi et al., 2018). In case of a combined sewer system, CSO includes untreated sewer from households and wastewater treatment plants, which can contain a lot of MPs from washing machine (fibers), personal care products (e.g., micro beads, mostly regulated today, Commission Regulation (EU) 2023/2055 2023), or wet wipes made from plastics (Ammendolia et al., 2021; Kooi et al., 2021; Nguyen et al., 2024). Household sewers usually would be treated in WWTPs where most of the MPs are redistributed to the sewer sludge, while the WWTP effluent would be less contaminated (Na et al., 2024; Nguyen, 2024; Tadsuwan & Babel, 2022; Talvitie et al., 2017).

Table 1–5 *Examples of common microplastic (MP) entry pathways to rivers categorized by spatial characteristics. Point and diffuse entry can occur temporarily or constantly.*

Point	Diffuse
Sewer overflow	Surface runoff
WWTP effluent outlet	Atmospheric deposition
Industrial discharge	Agricultural runoff
Stormwater outlets	Riverbank erosion
Spills	Tire and road wear particles (TRWP) runoff

1.3.2.3 Research gaps

Plastic fragmentation into MP is considered one of the major MP sources, but thus far, little is known about rates at which different plastics fragment under varying environmental conditions (Thompson et al., 2024). Most research focuses on urban MP release pathways, not sources per se. Incomplete mapping of pollution sources and limited cooperation between research, water quality authorities, and urban management hinder progress. For example, ship traffic and the influence on MP pollution in rivers is understudied. Only very few studies have included this topic in their work, even though paints and coatings are known to be important MP sources (Gaylarde et al., 2021; M. Wagner & Lambert, 2018). Although sewer discharges are one of the most widely studied pathways for the entry of MPs into rivers, the variability of MP pollution in relation to these inputs remains poorly understood. The investigation of diffuse and intermittent MP release is more difficult than that of continuous point release, particularly in the absence of regular monitoring. The role of various urban sources in contributing to riverine MP loads is still uncertain. The challenge remains to assess how much of the variation in riverine MP concentrations can be explained by MP release via urban discharge and other sources. This could help advance predictive MP models. Collaboration and data exchange are essential for advancing research on urban MP sources, and to improve monitoring and mitigation strategies.

Table 1–6 *Overview of common MP sources and entry pathways to rivers, and scientific studies that investigated the specific subjects.*

Source	Pathway to a river	References
Fibers, synthetic textiles	Release into wastewater during washing, release with wastewater treatment plant effluent and release via CSOs Release into atmosphere and atmospheric deposition	(Beaurepaire et al., 2021; Bujaczek et al., 2021; Dittmar et al., 2024; Dris et al., 2016; Kaliszewicz et al., 2020; Na et al., 2024; Rist et al., 2018; Said & Heard, 2020)
Automotive tire wear (Tire and road wear particles, TRWPs)	Surface and road runoff and wind transport	(Barber et al., 2024; Bondelind et al., 2020; Boucher & Friot, 2017; Unice et al., 2019)
Various (urban surfaces, litter, construction materials, TRWP)	Stormwater runoff from impervious surfaces	(Liu et al., 2019; Österlund et al., 2023; Ross et al., 2023; Treilles et al., 2021)
Various (households, industry)	Wastewater treatment plant effluent, untreated wastewater release/leakage, CSOs	(Bollmann et al., 2019; Imbulana et al., 2024; Nouraddin Ghanbari Tapeh et al., 2022; Schmidt et al., 2020; Waldschläger, Lechthaler, et al., 2020; Woodward et al., 2021)
Agriculture (MPs from sewer sludge, mulch)	Surface runoff, drainage water, soil erosion, wind deposition	(Khalid et al., 2023; Lwanga et al., 2022; Rehm et al., 2021; van Schothorst et al., 2021)
Various (see also the other examples)	Combined sewer overflows (CSOs)	(Bollmann et al., 2019; Dris, Gasperi, & Tassin, 2018; Nguyen et al., 2024; Schernewski et al., 2020)
Paints and coatings (ships, infrastructure)	Direct release during abrasion or via runoff	(Brännström et al., 2023; Faber et al., 2021; Gaylarde et al., 2021; Paruta et al., 2022)

1.3.3 UNDERSTANDING MICROPLASTIC FATE IN RIVERS

On the first level of microplastic (MP) fate in rivers stands the MP entry. The MP sources and processes triggering MP release and mobilization and the entry pathways as discussed in section 1.3.2 are important factors, determining where and when MPs enter. The fate of MPs in the river is influenced by a multitude of factors, including the MP material and particle properties and environmental conditions including urban river management and river characteristics (Table 1–7) (Akdogan & Guven, 2024; Domercq et al., 2022; Skalska et al., 2020; Waldschläger, Born, et al., 2020). The interplay of those factors determines the fate of an MP particle. Due to the complex nature of MPs (see section 1.2) and the varying environmental conditions in rivers, MP fate assessment is difficult. Research is trying to provide concrete answers to questions like: How are MPs transported in a river once released? How do MPs mix, resuspend, or settle within a river system?

Table 1–7 *What determines MP fate in a river?*

MP particle properties	Environmental conditions
Size	River management
Shape	River hydrodynamics
Density and material composition	River morphology and heterogeneity

1.3.3.1 MP particle behavior

The MP fate in a river can be described by processes of transport, transformation and environmental interaction and can be linked to the source-pathway-receptor model for environmental pollutant assessment. The development of multiple conceptual models of MP fate in rivers has been made possible by latest advances in science (Besseling et al., 2017; Buschman et al., 2020; Domercq et al., 2022; Kooi & Koelmans, 2019). The following paragraph is based on the references (Buschman et al., 2020; Domercq et al., 2022; Waldschläger, 2020; Waldschläger, Born, et al., 2020; Waldschläger & Schüttrumpf, 2019).

An MP particle can be moved or reallocated in three dimensions. In rivers, however, MP movements are linked to specific processes. Movement with the water flow is called *advection*; vertical movements can be described as *settling* or *rising*, or as *vertical mixing*. Experiments have shown that MP particles can rise or settle a few centimeters per second under environmental conditions. Their position in the water is hereby strongly dependent on the particle density and the size, with high density MPs (heavier) more prone to settle. MP *deposition* describes the transition from the water phase to river sediments, in which MPs may be buried (*burial*), transported vertically along the sediment bed (*sediment transport*) or *resuspended* (remobilized back into the water phase). MPs can be retained in a certain environmental compartment (MP *retention*) or transported into other

environmental compartments (e.g., from water to sediment or an organism, or from a river to the sea). Transformation processes include fragmentation and degradation (see also section 1.2.2). Depending on the factors affecting MP particles, such as UV radiation, biofilm growth, or mechanical stress, fragmentation and degradation rates can vary. Both processes are expected to be slow (years). Interaction processes include the formation of aggregates with other MP particles (homoaggregation) or other suspended particles (heteroaggregation), and organisms (biofouling and de-fouling, ingestion, and excretion) and de-aggregation. Aggregation and de-aggregation depend on the likelihood of particles colliding and their ability to aggregate. Processes like aggregation, biofilm or fragmentation can further influence the particle density and lead to MP redistribution in the water column.

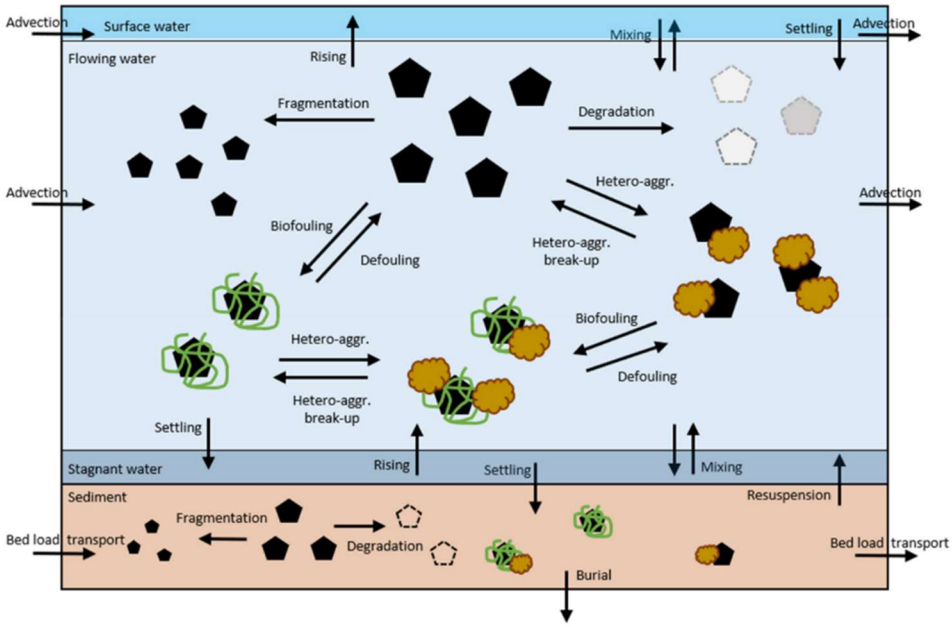

Fig. 1. Schematic representation of the Full Multi model unit cell and the fate and transport processes modelled in the water (applicable to surface, flowing and stagnant water) and sediment compartments. Black pentagons represent plastic particles, brown clouds are SPM and green scribbles are biofilm.

Figure 1–6 *Overview of MP fate processes in rivers. Figure from Domercq et al. (2022)*

1.3.3.2 Environmental conditions

Rivers are complex environments and there is a large variety of river types, from small alpine streams to large meandering rivers. Today, all European rivers are influenced by humans and are often highly modified (Schmutz & Sendzimir, 2018). River management and modifications include dams, locks, navigation channels, water diversion, or urban discharge infrastructure, all of which impact river hydrodynamics and morphology. Hydrometeorology is the study of the interaction between climate, weather, and catchment hydrology. It includes the effects of precipitation, wind, and temperature which affect infiltration and runoff in a catchment, controlling river flow and water levels.

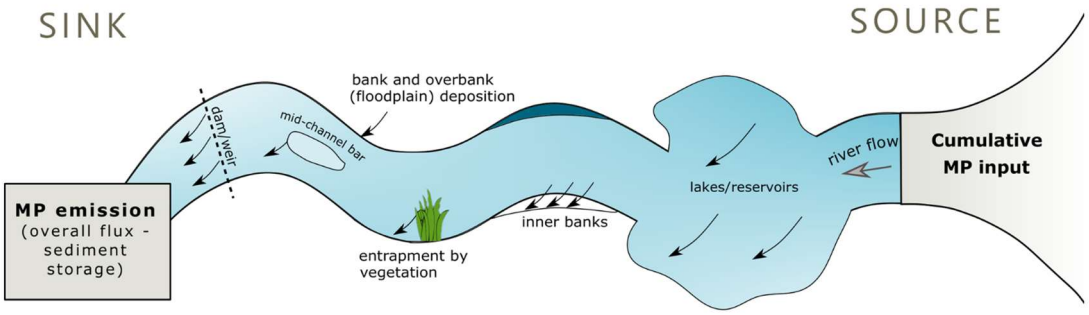

Figure 1–7 *From: Skalska et al. (2020). The figure illustrates the hypothetical capacity of a river to function as a microplastic (MP) sink related to physical variables associated with the heterogeneity of rivers. The arrows indicate areas where MP deposition is likely to occur.*

River flow is a key parameter that influences the fate of MPs (Skalska et al., 2020). In urban areas, river hydrology differs significantly from that in rural areas. For example, the percentage of sealed surfaces is much higher in cities, resulting in higher urban discharges, and straightened riverbanks allow less diversion and distribution of water masses leading to higher flow rates (Niemczynowicz, 1999). A higher river flow rate may lead to MP mobilization from riverbanks or via resuspension from sediments due to turbulence. Downstream increase of MP concentration (spatial gradient) can result from continuous inputs, mobilization in the river, and transport (Akdogan & Guven, 2024; Skalska et al., 2020), but many studies do not find a clear pattern (Erni-Cassola et al., 2024; Mani et al., 2019; Treilles et al., 2022). The rise in MP pollution along an urban river may also be attributed to the continuous discharge of MP, leading to its buildup and increased downstream transport. Heterogeneity in a river (e.g., variation in bank structure, morphology, vegetation, etc.) can also influence MP distribution (Skalska et al., 2020). Some studies have investigated the importance of location within a river by assessing MPs at different depths and across the river cross section (Dris, Gasperi, Rocher, et al., 2018; Erni-Cassola et al., 2024). MP advection was found to be stronger in calm river conditions than during turbulence, which rather increases MP mixing dynamics (Haberstroh et al., 2021). Turbulence in river water can influence the settling and rising of MPs in multiple ways, depending on particle properties such as shape and size, as well as river flow conditions (Akdogan & Guven, 2024; Dittmar et al., 2024). These hydrodynamic effects highlight that MPs are unevenly mixed in the water column, which complicates sampling and the interpretation of concentrations, fluxes or load estimates.

1.3.3.3 MP load approach

A MP flux or load approach (see also 1.3.1.2, Equation 1.3.1.2–1) provides a complementary quantitative measure of riverine MP transport (Kukkola et al., 2023). Load estimates help with understanding how MP masses move, e.g., from urban to downstream environments, and identifying MP inputs, the magnitude of emissions from sources, and enable better comparisons between different rivers. However, MP load calculations are inherently uncertain, as variations in flow and concentration can offset or amplify each other, and the approach assumes homogeneous MP distribution in the water body. Despite these limitations, flux or load assessments are a valuable tool for quantifying MP transport and inputs overall (Constant et al., 2020; Imbulana et al., 2024; Kukkola et al., 2023; Rios-Mendoza et al., 2021; Treilles et al., 2022).

1.3.3.4 Suspended solids as a proxy to understand MP fate

Beyond flow and concentration, the transport of MPs can also be examined in relation to other environmental parameters. Researchers are more and more interested in the relationship between MPs and suspended solids in rivers because of their potential physical similarities and shared transport mechanisms (Waldschläger & Schüttrumpf, 2019). The total amount of insoluble particulate material in the water column is represented as suspended solid concentration (SSC), including mineral particles, organic matter, and fine sediments (Dramais et al., 2018). SSC is commonly used as an indicator of erosion and sedimentation. Understanding the relationship between MPs and SSC can help to explain how MPs are transported, retained and mobilized (Range et al., 2023). For instance, watershed erosion and riverbank instability can contribute to MP resuspension, while hydrodynamic conditions influence whether MPs remain in suspension or settle (Akdogan & Guven, 2024; Kumar et al., 2021; Waldschläger, 2020). Similarities between MP and SSC were found for infiltration processes in the riverbed but not for other processes like resuspension from river sediment or settling and rising (Waldschläger, 2020). Other findings show that low-density polymers are sometimes found in sediments, despite being expected to float (Constant et al., 2020; Molazadeh et al., 2023). These differences demonstrate that, although SSC can be a useful proxy for understanding MP transport processes and link with river flow (Mohsen et al., 2023), MPs also follow distinct environmental pathways that are influenced by their polymer type, shape, and density. More research is needed to understand the relationship better and use the knowledge to inform MP fate dynamics. Investigating the relationship between MPs and SSC is essential, as MPs are particulate and SSC is easily measured. Expressing MP concentrations relative to SSC allows estimation of MP fluxes and parallel assessment of contamination in different solid matrices, providing a more universal tool for evaluating particulate pollution. In relation to that, MP can be determined as number of particles or mass per SSC linking back to the importance of different units to express MP pollution and comprehensive data reporting.

1.3.3.5 Research challenges

As mentioned in section 1.3.1 MP pollution research in rivers investigated spatiotemporal patterns in water, sediment, and organisms under environmental conditions. Previous research has focused on understanding seasonal differences governed by specific processes such as river flow. While testing detailed processes such as the transport of

MPs in riverbeds is complicated and typically addressed in laboratory experiments, field studies have focused on broader system-level dynamics. Assessing MP in relation to environmental parameters can help to test, support, or challenge existing hypotheses about MP fate and underlying processes. Great progress has been made in understanding the fate of MPs in rivers and conceptual models are being developed. However, there are still many uncertainties and many of the modelled relationships are based on assumptions and provisional knowledge (Buschman et al., 2020; Domercq et al., 2022). Processes such as deposition, sedimentation, biofilm formation or redistribution in the water column, can lead to complex MP fate and transport mechanisms (Buschman et al., 2020; Nizzetto et al., 2016; Waldschläger, 2020) of which many are not yet fully understood. There is currently a lack of standardized and comprehensive data to develop valid conceptual models of riverine MP fate. Thus, while machine learning approaches show promise, their application to predict MP dynamics in rivers is not yet feasible (Hu et al., 2024). Environmental fate models are based on datasets summarizing knowledge of particle behavior from controlled experiments and field observations. Advancing and calibrating existing models of MP dynamics requires valuable field data with good spatial and temporal resolution under environmental conditions (Kumar et al., 2021; Skalska et al., 2020). Some topics remain mostly unexplored to this day, such as the influence of temperature on MP fate in rivers (Kumar et al., 2021), but are potentially very relevant in the face of climate change (Quadroni et al., 2024). The interaction between catchment hydrology and the consequent triggering of diffuse and point releases of MPs, as well as river dynamics on both large and small scales in time and space, is complex and not yet fully understood.

1.3.4 MICROPLASTIC MONITORING

To understand and assess microplastic (MP) occurrence, fate, and impacts in rivers, field observations are necessary. MPs are not yet part of the array of parameters for regular water monitoring, but first regulatory frameworks to measure environmental MPs and develop risk assessments are underway (Thompson et al., 2024). However, due to the lack of regulation and the novelty of this contaminant, standardized monitoring or sampling methodologies for riverine MPs are not yet developed. The first environmental MP sampling was conducted at sea (Thompson, 2004) and more studies followed from around 2010 on (Browne et al., 2010; Cole et al., 2011; Imhof et al., 2012; Keller et al., 2010; Martins & Sobral, 2011; Moore et al., 2005, 2011). One of the first methodological reviews (Hidalgo-Ruz et al., 2012) identified two main problems: the variety of approaches and methods used to identify MPs, and the complexity of MPs (see also section 1.2). The scientific questions behind any study are linked to the monitoring approach and determine, for example, sampling locations or targeted MP types. This influences methodological choices (Figure 1–8). Other factors can be cost efficiency, availability of equipment, feasibility, site accessibility, safety requirements, or environmental conditions (see also section 1.3.3). For example: in a study researchers had to switched from large Manta trawl sampling to smaller conical net sampling due to high river flow (Constant et al., 2020). There are diverse approaches and methodological choices, but many studies contributed to harmonization (Gerdts, 2019; Kittner et al., 2022; Rochman et al., 2017; United Nations Environment Programme, 2020). Even though most studies are still following a unique

approach, there are certain similarities in sampling and analytical methods used. Prior to the final identification of MPs, including their quantification (number of particles) and qualitative characteristics, such as origin, color, shape, dimensions, degradation condition, chemical structure (i.e., polymer type), and more, sampling is required (Figure 1–9).

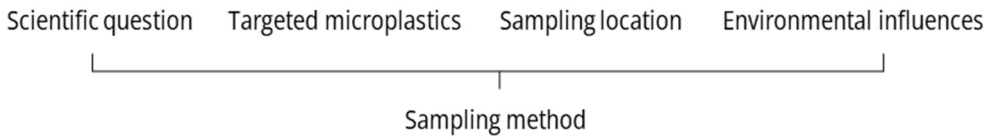

Figure 1–8 *The choice of the sampling methodology is influenced, a.o., by the scientific question and the MPs to be studies, as well as by the environment.*

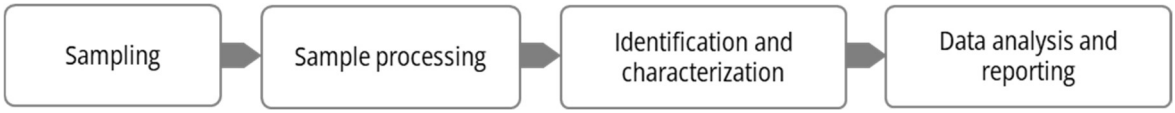

Figure 1–9 *The steps to be taken in order to evaluate MPs in the environment.*

1.3.4.1 Sampling methods

The rapid scientific progress over the last ten to 15 years has led to the development of and effort for harmonization of different MP sampling methodologies in river water and river sediment (Dris et al., 2024). In rivers, the cross section can be divided into different zones as visualized in Figure 1–10. Sampling methods target different zones: the water surface or surface microlayer (upper 1 mm), the water column, or the river sediment. There are two main strategies for MP sampling in water: volume-reduced sampling (filtered or sieved samples), or bulk sampling (unfiltered water sample) (Hidalgo-Ruz et al., 2012). Bulk sampling can also be combined with an *in-situ* sieving or filtration (Dris et al., 2024).

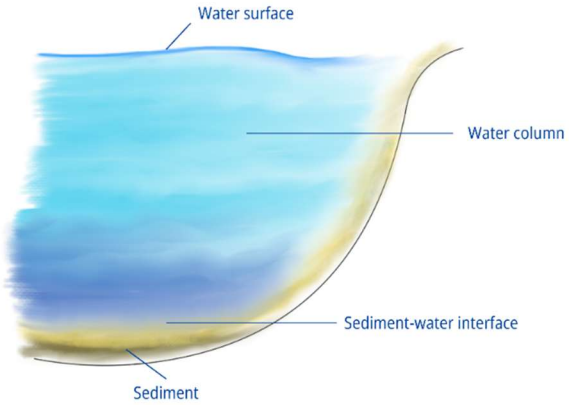

Figure 1–10 *A simplified generic river cross section and the different zones related to MP sampling. Modified from: Stratmann et al., (2020)*

Most commonly, bulk samples are taken using buckets, water bottles, or standard water samplers, like Niskin bottles (Figure 1–11). The collected bulk water is taken to further processing, or, when *in-situ* filtered, passed through a sieve at location. The disadvantage of bulk sampling is the logistical effort or transporting large amounts of water, limiting the sample volume to few liters and decaliters (Barrows et al., 2017; Mai et al., 2018). But the advantage is the ability to collect MP without any size limitation. The most common volume-reduced sampling methods are net trawling the water surface using a boat and vertical net sampling using zooplankton nets (Skalska et al., 2020). If there are enough current speeds in a stream, horizontal nets can also be fixed in place, often done from bridges (Dris, Imhof, et al., 2015). Mesh sizes of 300 µm or 330 µm are most common, originally derived from being zooplankton nets, but a variety of mesh sizes are used (Dris et al., 2024; Stock et al., 2022). River hydrological conditions like turbulences, waves or increased river flow can impact net sampling (Fahrenfeld et al., 2019; Klein et al., 2016; Stock et al., 2022). Another more common approach for volume-reduced sampling is *in-situ* filtration, either taking a bulk sample or using a water pump and filtering the water (Harrold et al., 2022; Tamminga et al., 2019). This is an effective method, and some plastic-free devices reduce potential contamination during sampling, which is a risk using open sampling devices. Some *in-situ* filtration systems use filter cascade systems, where water is passed through filters, sieves or nets of different sizes (Karlsson et al., 2020). The pump inlet can be inserted into the water at different depths and enable for a targeted sampling in the water column (Tamminga et al., 2019). These systems can be automated and up to several cubic meters per hour can be pumped (Stratmann et al., 2024). Automated water sampling systems are rarely used in river field studies but could offer effective sampling. Most automated systems used in continental waters are bottle-based setups, collecting a bulk sample. A few studies used different sampling methods like sediment traps, where the settling matter in the water, including MPs, are collected (Saarni et al., 2020, 2021). Sampling in river sediments commonly uses grab or core sampling techniques, each suited to different research aims (Frias et al., 2018; Stock et al., 2022). Grab samplers collect disturbed bulk surface sediments and are practical for field studies looking at spatial distribution of MP contamination. Sediment cores retrieve undisturbed, stratified samples, enabling the analysis of vertical MP distribution and historical deposition trends but are used less (Mai et al., 2018; Skalska et al., 2020; Van Cauwenberghe et al., 2015). The choice of sampling technique depends on study aims, sediment characteristics, and desired resolution.

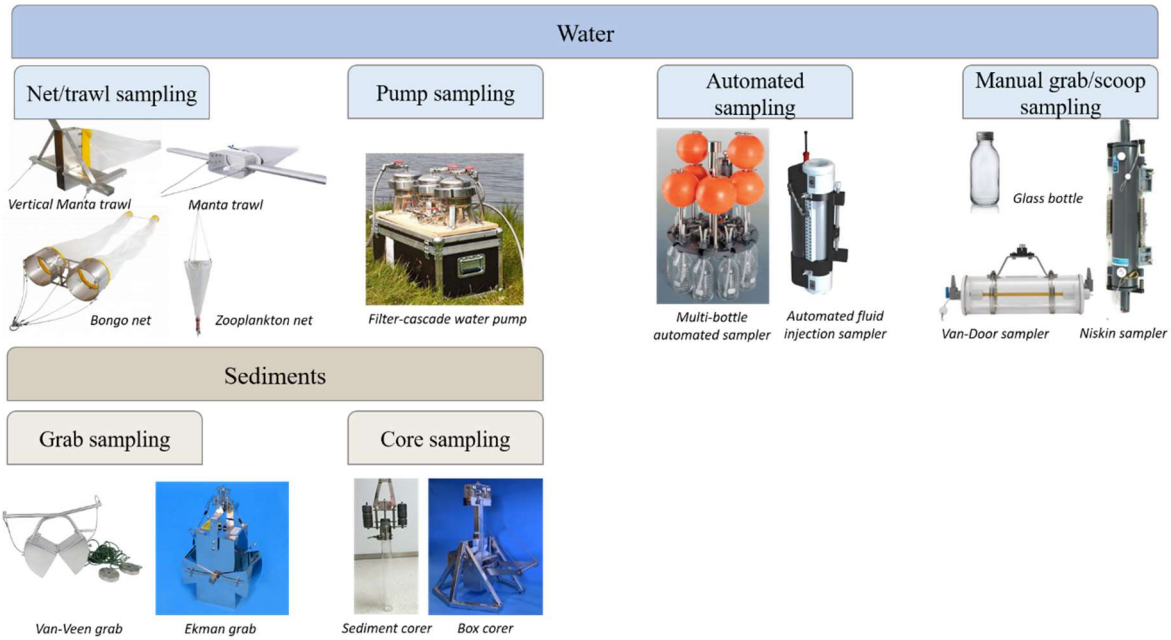

Figure 1–11 *Examples of microplastic sampling options in rivers for water and sediments. From: Stratmann et al., (2020)*

The limitations of the later MP assessment are pre-determined by the sampling method (Watkins et al., 2021). These include minimum and maximum particle sizes (cut-off), the probability of sampling MP of different shapes, sizes, and observing rare particles (taking the sampling volume into account), the potential for contamination, and the amount of laboratory sample processing required. Figure 1–12 gives a simple visualization of the factors which are intertwined with each other. The pressure and potential of clogging of nets or filters through suspended particles is higher with smaller mesh sizes, reducing the maximum sample volume and sample speed. Depending on the method used, different volumes of water samples can be taken, and different MP sizes can be obtained. The volume is important for ensuring that a sufficient number of MP particles are sampled, with larger particles and rare polymers being potentially underrepresented (Cross et al., 2025; Skalska et al., 2020). With scientific evidence of smaller MPs being more abundant, sampling MP with a low cut-off size is important. With less variance observed in data with larger sample volumes, it is recommended to determine the minimally required sample volumes during the study design and planning based on expected MP concentrations. Tools like the Representative Sample Volume Predictor (RSVP) can be used to help (Cross et al., 2025). Recommendations include clear phrasing of the study design, identifying important data, and inspection of its representativity for the research aim and approach.

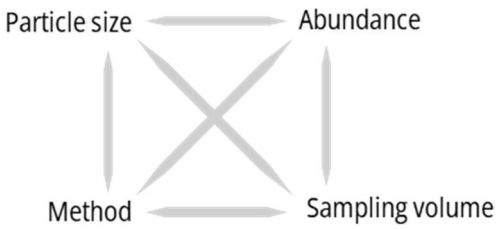

Figure 1–12 *The dependencies between sampling method, sampling volume, measured microplastic abundance and the particle sizes.*

1.3.4.2 Sample processing and particle identification

The main aim of sample processing is to extract MPs from the environmental matrix (Figure 1–13). The process of preparing samples often includes ways to break down organic substances, methods to separate inorganic material from MPs, and filtration (Dris et al., 2024). Hereby, the handling of samples influences the precision of the MP identification. For the breakdown of organic matter different techniques can be applied, such as enzymatic digestion using specific enzymes, such as cellulase, lipase, and chitinase (Löder & Gerdts, 2015). These processes occur at specific temperatures and pH levels and are useful for samples containing high amounts of organic material, such as wastewater or sediments (Dris et al., 2024; Nguyen et al., 2024). In contrast, chemical digestion techniques are commonly used in river water samples, using oxidizing, acidic, or alkaline solutions (e.g., H_2O_2, HCl, or KOH) (Treilles et al., 2020). However, chemicals may alter some polymers. For example, reducing organic matter using chemicals such as hydrogen peroxide has the potential to alter the color of some particles and can lead to the degradation of certain polymer types, making them appear more aged in later identification (Löder & Gerdts, 2015; Treilles et al., 2020). To reduce such biases, it is recommended to keep sample processing to a minimum (Stratmann et al., 2020), and steps may be skipped if samples are clean. For samples with high inorganic matter percentage or sediment samples, density separation is applied. A mid-density solution like NaCl, ZnCl is prepared and added to the sample (Hidalgo-Ruz et al., 2012; Imhof et al., 2012; Ivleva et al., 2017). MPs with a lower density than the solution float up while heavier (high-density) particles, including most inorganic particles, sink. This separation process is typically performed in separation funnels (Nakajima et al., 2019). A very important subject in sample processing is the verification of a method's efficiency and estimation of the recovery rate (Dris et al., 2024). A common approach is the parallel treatment of blank samples (samples without MPs) or the treatment of spiked samples (samples with known number and types of MPs). While blanks are more commonly conducted, spiking remains a challenge due to accuracy and is rarely used (Quinn et al., 2017; Tagg, 2023).

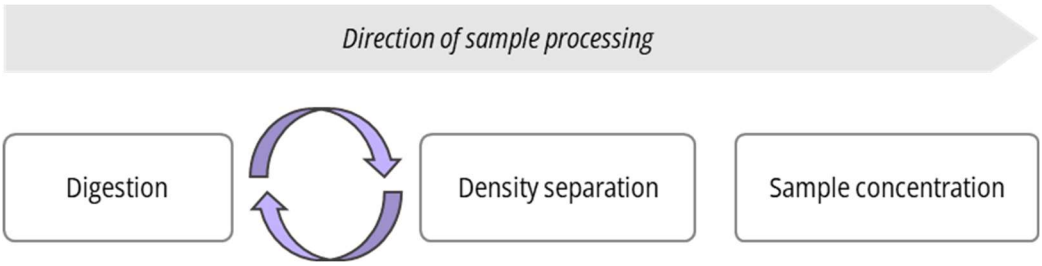

Figure 1–13 *Microplastic (MP) sample processing*

After sample preparation MPs can be identified and quantified using an array of methods and instruments. Depending on the targeted size class and polymers, these methods must be selected carefully, as some are destructive (e.g. mass-spectrometry methods), destroying the sample in the process (Bouzid et al., 2025). Other methods keep the sample intact, enabling it to undergo further analysis, re-analysis, or storage. Recommendations for MP size subclassification is based on the visual ability to identify by eye (MP > 1mm) versus smaller MPs where optical methods are needed (MP < 1mm) (Dris, Imhof, et al., 2015). Most commonly applied are visual inspections for larger MPs, and spectrometric methods like Fourier transform infrared spectrometry (FTIR) or Raman spectrometry (or both), allowing also for chemical characterization of particles (Käppler et al., 2016; Löder & Gerdts, 2015; Thompson, 2004). Those approaches are measuring particles numbers, while other techniques are mass-based, like pyrolysis-gas chromatography coupled to mass spectrometry (Py-GC-MS) (Fischer & Scholz-Böttcher, 2017; Fries et al., 2013). For spectrometric methods, the results are then compared to reference spectra. Reference library comparison usually works based on probability thresholds assigning the highest probability score belonging to a polymer (e.g., PE and above the threshold, e.g., 75%). Other methods are developed, like hyperspectral imaging (Faltynkova et al., 2021; Fiore et al., 2022), and are gaining interest in research, but access to knowledge and instruments and other resources is a limiting factor, as well as lack of harmonized or standardized guidelines. Visual and manual inspection is usually done with binocular microscopes (Fries et al., 2013), or stereo microscopes (Barrows et al., 2017), but the manual handling and low efficiency is a common issue (Löder & Gerdts, 2015). Nile red is another method often applied for some common polymer types and larger-size MPs. Particles fluoresce under blue light and can be counted under microscopes. But staining agents are not specific for certain types of MPs and false positives may occur (Hengstmann & Fischer, 2019; Ruggero et al., 2020).

1.3.4.3 Research challenges

The use of a wide array of sampling techniques throughout the studies hampers comparability which is a common issue (Dris et al., 2024; Scherer, Weber, et al., 2020). Comparing various studies and understanding MP pollution in rivers requires regular and spatially relevant monitoring, harmonized, valid analytical methods, and transparent reporting (Löder & Gerdts, 2015). The exposure of MPs to different conditions (temperatures, chemicals) and the handling by multiple people, plus the multitude of processing steps are risk points for contamination and biases. A list of further recommendations is provided in Stratmann et al. (2020). Even within a single study using

the same sampling and/or identification methodology, MP concentrations can vary widely (Becker, 2020; Ciornii et al., 2025; Dris et al., 2024; Elert et al., 2017; Kukkola et al., 2024; Sefiloglu et al., 2024; Song et al., 2015; Stratmann et al., 2025). The assessment of the reliability, detection limits, and performance rate of a method itself is necessary under controlled conditions, such as a calibration approach and standardization is urgently needed (D'Avignon et al., 2022; Dris, Imhof, et al., 2015; Thompson et al., 2024).

CHAPTER 2 STUDY AREA AND AIMS

This chapter presents the study area where the research has taken place and links the research challenges in the scientific field to this case study in Paris. The aims and research questions of this thesis are stated.

2.1 THE SEINE RIVER IN GREATER PARIS

France is a European country with ~68 million inhabitants[2], ~13% of which (~9 million) live in Greater Paris (included in the region *Île de France*). The region has a temperate climate with oceanic influence, warm summers, mild winters, and stable precipitation throughout the year (annual average 641 mm). Greater Paris holds about 25% of the gross domestic product in France. It is an economic center for industries engaged in the production and export of food, beverages, plastics and mineral materials, machinery, textiles, and more[3]. Anthropogenic activities include urban development, industrial operations, and agriculture. The main rivers in Greater Paris are the Seine, Marne, Yonne, Oise, and Essonne[4], of which the Seine, Marne and Oise are also navigable.

The Seine River has its source in the Dijon plateau (east France) and flows ~750 km north-west into the English Channel, passing through Paris. The Seine River catchment area covers around 77,000 km^2 with about 17 million inhabitants. The catchment is economically very important, because of international navigation, the supply of drinking water in Greater Paris, and irrigation for the agricultural sector (Tabuchi et al., 2018). Compared to other French rivers such as the Rhône, the Seine is smaller but is affected by a larger population (Table 2–1). The average river flow is ~300 $m^3 s^{-1}$ measured in Paris city and ~600 $m^3 s^{-1}$ at the outlet before the estuary (Poses).

[2] https://european-union.europa.eu [accessed on October 28, 2025]

[3] https://www.prefectures-regions.gouv.fr/ [accessed on July 06, 2024]

[4] https://www.prefectures-regions.gouv.fr [accessed on October 28, 2025]

Table 2–1 *The Seine River on the scale of the Île-de-France in comparison to rivers Rhine and Rhône. From: Tabuchi et al. (2018)*

Table 3. Comparison of minimum water flows and dilution capacity of different French rivers

	Five-year minimum water flow	Conurbation	Population	Impacts
	m^3/s		Millions of inhabitants	Dilution capacity
Rhine	520	Strasbourg	0.7	65 m^3/d/inhabitant
Rhône	380	Lyon	1.8	18 m^3/d/inhabitant
Seine (at Poissy)	170	Paris urban unit	10.5	1.4 m^3/d/inhabitant

The river flow, naturally influenced by precipitation and evaporation, is typically low between March and October and higher during the winter months, when floods are common. Winter floods often develop gradually, with flow increasing and decreasing slowly over roughly one month, as observed in the past (flood years: 1910, 1924, 1955, 1982, 1999–2000, 2016, 2018)

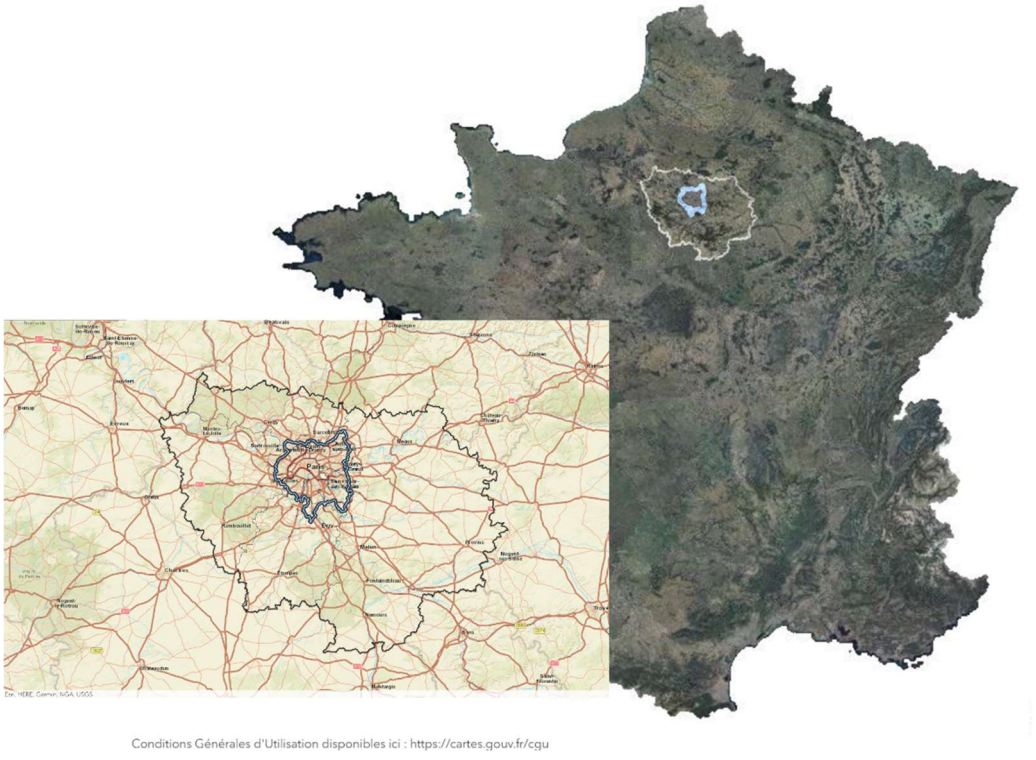

Figure 2–1 *The region Île-de-France (larger perimeter) and Greater Paris (smaller perimeter) in France. Map made with: ESRI and data from cartes.gouv.fr, HERE, Gemini, USGS*

Also droughts (due to low precipitation and high evaporation) are not uncommon in the Paris region, and they are becoming increasingly problematic as climate change leads to more prolonged dry periods and reduced river flows. This results in restrictions on water use and climate change scenarios indicate groundwater levels could drop by up to 12 meters (OECD, 2025). In the 1990s, river management was achieved and four upstream

reservoirs called '*The Seine Grands Lacs*' with storage of about 850 million m^3 were built. These reservoirs help to control the river flow in summer (to be kept above 100 $m^3 s^{-1}$) and to prevent floods.

Since the late 19th century, sewage and agricultural pollution have led to worsening of the Seine water quality. But improvements in sewage and stormwater infrastructure were made in the 1970s (Tabuchi et al., 2018). Today, the Seine River has a moderate water quality status (regarding the Water framework directive) and upon 2025 some bathing sites in the Seine in Paris were opened (OECD, 2025). Nonetheless, the water in the Seine River is under enormous pressure, and climate-induced droughts and lower river flow could lead to a deterioration in water quality by 2050 (OECD, 2025; Tabuchi et al., 2018). Today, the Seine River is exposed to multiple stressors, including plastic pollution, urbanization, extreme weather, nutrient and pesticide inputs, organic pollutants, and sewer inflows (Flipo et al., 2021; Tabuchi et al., 2018; van Emmerik et al., 2019; Vilmin et al., 2015).

The urban sewer network in Greater Paris is managed by the greater Paris Sanitation Authority (SIAAP – Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne) managing wastewater for about 9 million people (Tabuchi et al., 2018) at six wastewater treatment plants (WWTPs). On average, 60% of the treated wastewater is domestic wastewater, 25% is infiltration water, and 10% is stormwater and about 8% is other non-potable water. The WWTPs in Greater Paris continuously discharge around 800 million m^3 of effluent per year. The 15,000 km network for wastewater and stormwater of Greater Paris includes combined (2,100 km) and separate sewer networks. Over 80% of the space in the center of Greater Paris is built space (Tabuchi et al., 2018). In this densely populated conurbation with a high percentage of sealed surfaces, urban stormwater infrastructure is important (OECD, 2025). Depending on precipitation, between 10 – 20 million m^3 of CSO effluents are discharged at the scale of Paris into the Seine River annually. Despite stormwater storage facilities and the introduction of Real-Time Control, CSOs happen in Paris regularly. In the case of Paris, there are ~200 CSO stations flushing sewer pipe sediments, debris, and pollutants including MPs directly into the Seine in the event of an overflow (Tabuchi et al., 2018). Twelve of the CSO locations in Paris together are responsible for 91% of the CSO, and two sites, Clichy and La Briche, together make about 50% of all CSO.

Urban discharges are a major MP entry pathway to rivers, underscoring the potential towards MP pollution in the Seine. Several studies confirmed the contribution of MPs via urban discharges into the Seine from stormwater runoff, WWTP effluent and CSO (Dris, Gasperi, et al., 2015; Nguyen et al., 2024; Treilles et al., 2021). In 2015, a study scaled over Greater Paris (Dris, Gasperi, et al., 2015) determined MPs in raw (up to 320×10^3 particles m^{-3}) and treated wastewater (up to 50×10^3 particles m^{-3}) with mostly fibers. They estimate that up to 45 tons of MP fibers are released via WWTPs effluent to receiving water annually. Nguyen et al. (2024) estimated between 203 – 48×10^3 MP particles m^{-3} entering the Seine from CSO. CSO outflow at La Briche was found to contain 160×10^3 particles m^{-3} and at Clichy 137×10^3 particles m^{-3} (Dris, Gasperi, et al., 2015). Stormwater was found to contain up 29×10^3 particles m^{-3} (median).

MPs have been investigated in different parts of the Seine (Table 2–2) and the levels vary between studies but are similar to what was found in other European rivers (Table 1–4). In the Seine catchment and Greater Paris, the most studied MP subjects were atmospheric deposition, runoff, urban wastewater, river water and river sediments. In deposit from the river bank, MPs up to ~50 particles g^{-1} dry sediment were found (Bouzid et al., 2025). The surface waters in Paris might receive up to 0.1 tons of MPs via atmospheric fallout. In the surface water, MPs [>80 µm] were found between 3 – 106 particles m^{-3} MPs [>300 µm] in lower abundance between 0.3 – 0.5 particles m^{-3} (Dris, Gasperi, et al., 2015). Spatial and temporal dynamics were observed and some could be attributed to flood events (Treilles et al., 2022). They observed MPs in the Seine water under flood conditions of 16×10^3 particles m^{-3} (median) and approximated the annual load of MP between 58 – 1675 tons $year^{-1}$. When MPs were compared from upstream and downstream Paris, the studies found less pollution upstream, and there were observations of increased MP concentration with river flow, but no significant spatiotemporal patterns (Dris, Gasperi, et al., 2015; Treilles et al., 2022). A other studies investigated MPs form tire and road wear and found natural rubber and SBR to be present (Barber et al., 2024).

Table 2–2 *Microplastic levels in the Seine River water, sediments, and in urban discharges in Greater Paris (France)*

	Study	Compartment	MP information	MP sizes	Reference
Water	m	Seine river water	Range : 3 – 106 particles m^{-3} Mean: 30 particles m^{-3}	80 µm – 5,000 µm	Dris et al. 2015
			Range: 0.3 - 0.5 particles m^{-3} Mean: 0.35 particles m^{-3}	> 330 µm	
	n	Seine river water	Median: 15,500 particles m^{-3} Range MP mass flux: 924 – 1,675 *[t yr^{-1}]*	> 80 µm	Treilles et al. 2022
	q	Seine river water	Range: 330 – 5920 mg kg^{-1} (rubber)		Barber et al. 2024
Urban discharges	r	CSO in Paris	Range: 203 – 48x10^3 particles m^{-3}	25 – 500 µm	Nguyen et al. 2024
	r	Sewer sediments	Range: 5 – 178 particles g^{-1} DW	25 – 500 µm	Nguyen et al. 2024
	s	Stormwater runoff	Median: 29x10^3 particles m^{-3}	80 – 4,000 µm	Treilles et al. 2021
	m	Raw and treated wastewater	Maximum raw: 320 x10^3 particles m^{-3}; maximum treated 50 x10^3 particles m^{-3}	80 µm – 5,000 µm	Dris et al. 2015
	m	CSO in Paris	Median La Briche: 160 x10^3 particles m^{-3}; median Clichy 137x10^3 particles m^{-3}	80 µm – 5,000 µm	Dris et al. 2015
Sediment	p	Seine river sediments	Up to ~50 particles g^{-1}	25 – 500 µm	Bouzid et al. 2025

2.2 AIMS AND RESEARCH QUESTIONS

There is a gap in comprehensive *in-situ* data of river microplastics (MPs) and a lack of understanding MP sources, fate, and ecological impacts. In addition, methodologies of MP assessment are continuously evolving in this new research field, causing incoherence among research studies and making results difficult to compare. In the past ten years MPs down to 80 µm but mostly above 300 µm were investigated in the Seine River. There is yet a complete picture to draw and to be kept up to date, ultimately to report on levels of contamination and inform mitigation measures. Improvements in sampling and analytical methods for MPs make it possible to measure higher quantities with higher quality (so, more precision). This brings me to the **first aim** of this thesis: to fill the data gap and extend the knowledge of smaller-sized microplastics in the Seine River in Greater Paris. This includes quantification of MPs between 25 – 300 µm, to understand MP fate in the Seine catchment and how much Paris contributes to the pollution. The **second aim** is to answer questions related to methodological choices when investigating MPs in rivers. The overall goal of this thesis is to contribute knowledge and insights of the abundance, sources, and sampling methods of microplastics in rivers in urban areas, specifically in the Seine River.

Research question 1: *What is the abundance of small microplastics in the Seine River in the Greater Paris area under different river flow conditions* ***(paper I and II)****?*

This question was approached by assessing microplastic contamination in the Seine River up- and downstream of Paris **(paper I and II)**. Therefore, larger field sampling campaigns were conducted during different flow seasons.

Research question 2: *What is the contribution of the Paris metropolitan area to the microplastic contamination in the Seine River* ***(paper II)****?*

In addition to RQ 1, microplastic data was analyzed in relation to rainfall, wastewater treatment plant (WWTP) effluents and combined sewer overflows (CSOs) discharge data as potential microplastic sources **(paper II)**.

Research question 3: *Is the method of microplastic sampling important to assess microplastics in the surface water of rivers* ***(paper III, IV and V)****?*

To answer this RQ, a comparative high-frequency sampling was conducted using two different sampling methods **(paper III)**. In addition, a literature review **(paper IV)**, a standard operating procedures document (**paper VI**), and a collaborative study **(paper V)** using one of the sampling methods in Amsterdam canals support this part.

2.3 METHODOLOGICAL APPROACH

This PhD thesis is cumulative work including three articles of which one has been published in a peer-reviewed journal, one is ready to be submitted for peer-review, and one is a manuscript. In addition, a contribution has been made to a peer-reviewed book chapter, a peer-reviewed research study, and a standard operating procedure (SOP).

The PhD study addressed three main parts:

- Investigation of the occurrence and fate of small microplastics (MPs) in Seine River in low flow and high flow conditions
- Assessment of the impact of urban discharges on MP abundance in Paris
- Assessment and comparison of methods to sample MPs in the upper water layer of a river

The first topic was addressed via MP monitoring over the course of one year at multiple sites in the Seine River from upstream to downstream of Paris. This included sampling, laboratory analysis, MP identification, and data interpretation. Topic two was addressed by combining third-party data of CSO, WWTP effluents and precipitation with the microplastic field observations and assessment in relation to hydrometeorological river conditions. The third part was approached in two-fold: a high-frequency MP sampling and a synchronized parallel sampling were conducted at a location in the Seine, comparing an *in-situ* pump filtration set-up to a settling trap. In addition, a review of methods and a comparable field study are included.

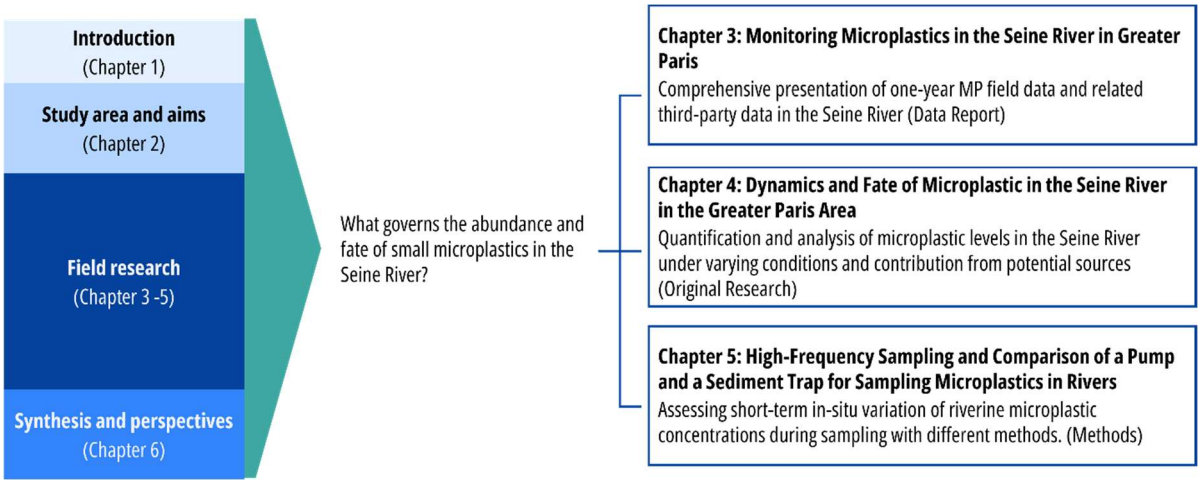

Figure 2–2 *Structure of this PhD thesis and chapters.*

The first paper comprehensively reports on data from the one-year MP monitoring within the Greater Paris area. It includes sampling data on MP concentration, water parameters, third-party hydrometeorological data, as well as data from urban discharge sources (WWTPs, CSOs) within Greater Paris. The MP load in the river was quantified, and a first preliminary data analysis is presented. The dataset provides first insights into MP pollution in direct comparison with direct discharge data from potential MP sources.

In the second paper, the abundance of MPs including different polymer types and sizes in the hydrometeorological and urban context of upstream, within the center and downstream of Paris and discussed the findings with relevant literature. First, the MP abundance under different flow regimes was assessed to understand MP dynamics and local differences along the Seine, over time and space. Then, the MP levels related to urbanization (from upstream to downstream), and the MP characteristics (polymer type and particle sizes) were investigated. MP pollution loads were estimated and a mass balance was presented followed by a source-fluxes analysis to assess the influence of urban discharges on MP pollution. The influence of urban sewer discharge on the observed MP load in the Seine was analyzed over space and time to gain important insights into MP inputs via those pathways.

In the third paper, a high-frequency MP field sampling with comparison of two sampling methods is presented. The purpose of this study was to assess the *in-situ* variation of MP data during sampling and to analyze methodological differences between a pump and sediment trap sampling device. Methods to sample MP concentration vary across studies and within studies, making comparison of data and the right choice of method more difficult. While studies are often compared, it is important to understand the differences as this determines the results. MPs are not homogeneously distributed throughout the water column in a river. Variation at the first step of data acquisition, i.e., sampling, is a factor that sets the basis for the quality of the results. Hence, it is important to understand the variation during field sampling in rivers, a factor that has not been researched extensively yet.

CHAPTER 3 MONITORING MICROPLASTICS IN THE SEINE RIVER IN THE GREATER PARIS AREA (PAPER I)

Published article, Article type: Data report

Stratmann CN, Dris R, Gasperi J, Buschman FA, Markus AA, Guerin S, and Tassin B *Monitoring Microplastics in the Seine River in the Greater Paris area.* Front. Earth Sci. (2024)

A *Corrigendum* has been submitted to the journal and is under review. The version in this thesis is corrected.

The authors regret to inform readers of a mistake in the units of microplastic mass concentration in the original manuscript and the attached database. Mass concentration units were reported incorrectly by a factor of 1,000. Hence, units were corrected throughout, for example mg was changed to µg. The authors would like to apologize for the inconvenience.

Monitoring Microplastics in the Seine River in the Greater Paris area

Cleo N. Stratmann[1]*Rachid Dris[1]*Johnny Gasperi[2]Frans A. Buschman[3]Adriaan A. Markus[3]Sabrina Guerin[4]A. Dick Vethaak[3,5†]Bruno Tassin[1]

[1]Laboratoire Eau Environnement et Systèmes Urbains, Ecole des Ponts ParisTech, Université Paris Est Créteil, Marne-la-Vallée, France
[2]Laboratoire Eau et Environnement GERS-LEE, Université Gustave Eiffel, Bouguenais, France
[3]Deltares, Delft, Netherlands
[4]Syndicat Interdépartemental pour l'Assainissement de l'Agglomération Parisienne (SIAAP), Paris, France
[5]Amsterdam Institute for Life and Environment (A-LIFE), Vrije Universiteit Amsterdam, Amsterdam, Netherlands

Abstract

This data paper presents microplastic (MP) concentration and composition data from four campaigns in a one-year period in the Seine River within the Greater Paris area. Detailed data on MP occurrence, physical water parameters, hydrological conditions, and potential sewer point sources are presented. Initial analysis of the data set shows that MP concentrations were significant (median: 600 particles m^{-3} and 100 µg m^{-3}) and MP fluxes showed variations across sampling sites and campaigns. Three polymer types (polypropylene - PP, polyethylene - PE, polystyrene - PS) account for 96% of the total number of MP. This dataset provides valuable insights for understanding river MP pollution under anthropogenic pressure.

1 Introduction

Microplastics (MPs) are ubiquitous environmental contaminants present in all natural compartments (Miranda et al., 2020). MPs are persistent and harmful, e.g., through the release of toxic chemicals (Wagner et al., 2024), negatively impact natural resources, organisms, and human health (Amobonye et al., 2021). It is thus important to understand MP fate and impact once they leaked into the environment to adopt mitigation and protection measures. Freshwaters are key ecosystems worthy of protection against MP pollution and rivers play an important role. Rivers are often under anthropogenic pressure receiving MPs (Kumar et al., 2021) through surface runoff, combined sewer overflows (CSOs), or wastewater treatment plant (WWTP) effluent (Fahrenfeld et al., 2019; Nguyen et al., 2024). To elucidate sources, understand MP transport and assess the ecological impacts comprehensive monitoring is needed. This should include MP concentration and fluxes (Miranda et al., 2020) across temporal and spatial scales like in a recent study on microplastics in canals of Amsterdam (Sefiloglu et al., 2024). Additional information on the environmental conditions such as the river flow rate, weather conditions, and water quality parameters like suspended particle concentration or algal biomass help to explain MPs in the environmental context (Birch et al., 2020) and to identify potential solutions (Li et al., 2020; Li et al., 2023).

The Seine River in France (Figure 1) meanders 750 km from east to northwest and is subject to intense urban activities (up to 5,000 inhabitants km^{-2}) before reaching the English Channel. Traversing Greater Paris with 12 million inhabitants (Tabuchi et al., 2016) the Seine consistently receives sewer effluents via WWTPs (2021: ~853 million m^3 from four major WWTPs) and CSOs (~23 million m^3 in 2021) during periods of intense rainfall (Flipo et al., 2020, 2021). Studies (Dris

et al., 2015; Treilles et al., 2022) have highlighted MP contamination in the Seine around Paris, exhibiting 4–5,000 particles m^{-3} as median concentration.

Further insights into the complex dynamics of MP occurrence in the Seine River are needed. This data paper is the basis for further analyses presented later answering questions like: Are MP concentrations increased downstream of Paris, indicating significant urban contribution to the contamination and which urban sources could be important contributors? How is MP occurrence linked to the different MP sources along the river stream?

Therefore, a 1-year MP monitoring campaign in the Seine River upstream and downstream of Greater Paris was conducted. This paper describes the unique MP monitoring dataset of the Seine River including 1) an overview of MP occurrence in the Seine between July 2021 and July 2022 based on four sampling campaigns, 2) data on physical water parameters, 3) data on hydrological conditions including a water balance, and 4) data on potential sewer point sources. This dataset provides comprehensive data reporting to foster cross-study comparisons (Cowger et al., 2020).

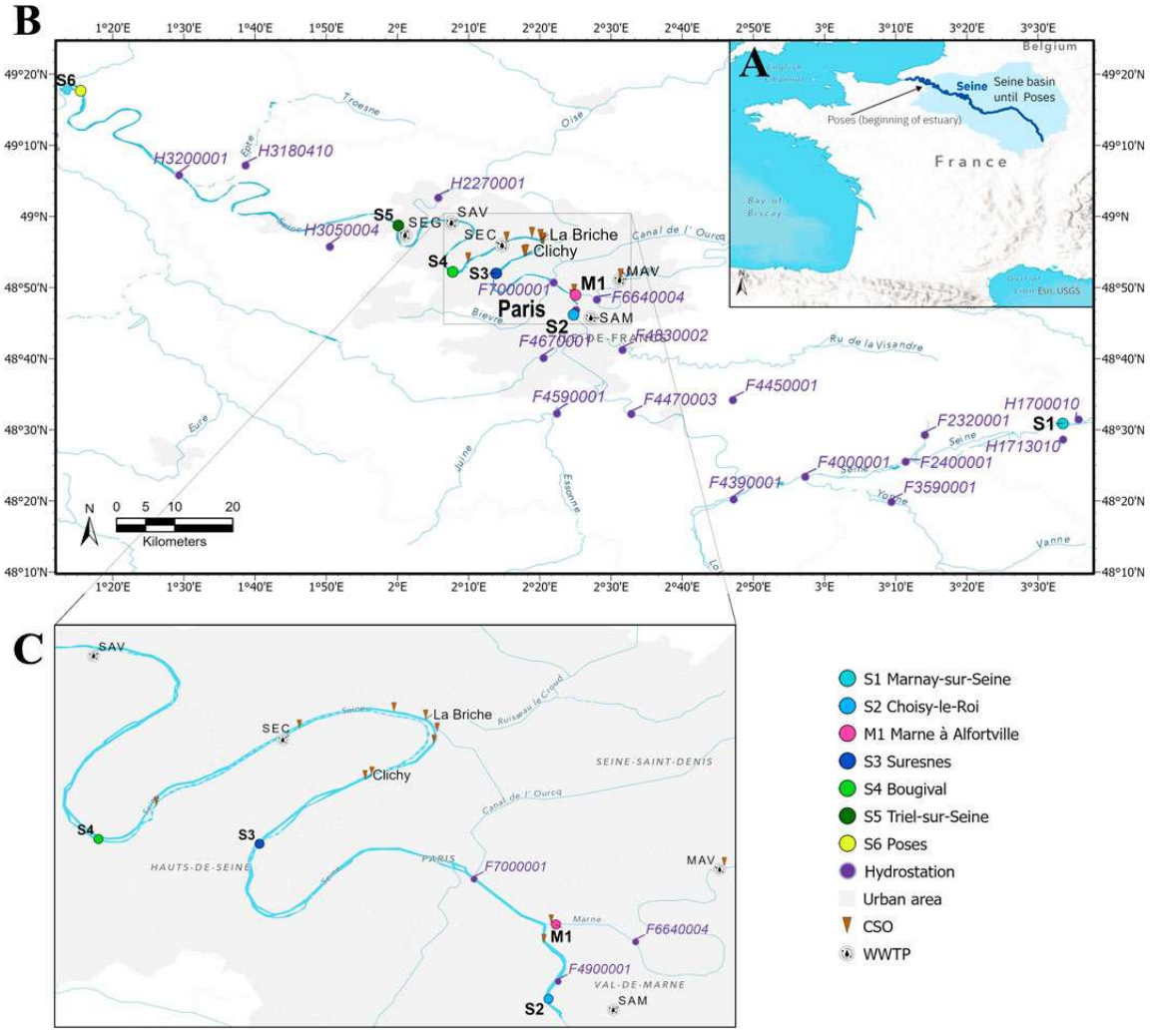

Figure 1. **(A)** Map of France with the Seine River and the Seine basin until Poses before the estuary starts (light-blue area). **(B)** Map of the monitoring area showing Seine River catchment situated in Northern France and the sampling sites (S1-S6 and M1), urban area is defined as functional urban area (OECD, 2012), hydrological measurement stations (Hydrostation labeled with identifiers), combined sewer overflow (CSO) locations (sites La Briche and Clichy hold >50% of the

discharge volumes in Paris), and wastewater treatment plant (WWTP) locations SAM, Seine Amont; MAV, Marne Aval; SEC, Seine Centre; SAV, Seine Aval; SEG, Seine Grésillons. **(C)** Magnification detailing CSO sites that each exhibit >1% of the annual CSO discharge volume (see metadata in the Supplementary Material).

2 Methods

Monitoring included collecting MP data and some physical water quality and hydrological parameters from field samples and measurements. Detailed hydrological and meteorological data (river discharge, water level, precipitation) and data on sewage discharges (WWTPs, CSOs) were collected by third parties.

2.1 Monitoring

2.1.1 Sampling sites and monitoring period

The monitoring area (Figure 1A) is situated in the upper Seine catchment (~67 × 10^3 km^2). The oceanic climate has annual average temperatures of 19.5°C in summer and 5°C in winter, with low temporal variations in rainfall (mean annual precipitation 642 mm). The Seine (mean discharge in Paris: 319 m^3s^{-1}) has two distinct seasonal flow regimes: a low flow during summer (mean 125 m^3s^{-1}) and a high flow during winter (mean 583 m^3s^{-1}) (Flipo et al., 2021). This seasonality is driven by evapotranspiration in the catchment and the presence of natural aquifers. Four upstream reservoirs maintain summer flows above 100 m^3s^{-1} and contribute to regulate flood periods. Twelve tributaries flow into the Seine within the monitored area, including the three preeminent tributaries Yonne, Marne, and Oise. Six sampling sites reached downstream spanning 442 km along the Seine from Marnay-sur-Seine to Poses before the estuary influence (Figure 1). The two sampling sites Marnay-sur-Seine (S1) and Choisy-le-Roi (S2) are located upstream of Paris, and four sampling sites at the locations Suresnes (S3), Bougival (S4), Triel-sur-Seine (S5), and Poses (S6) are located downstream of Paris. An additional sampling site just before the Seine-Marne confluence at Marne à Alfortville (M1) was monitored to account for MPs entering from the Marne River. All sampling sites exhibited anthropogenically modified riverbanks varying from concrete walls to overgrown slopes. Two sampling campaigns per river flow season (low and high) were carried out. The four sampling campaigns were conducted in July 12–22, 2021, November 2–11,2021, February 15- 24, 2022, and July 20–27, 2022.

2.1.2 Sample and data collection

2.1.2.1 Microplastics

MPs with a major particle diameter between 25 µm and 300 µm were assessed. The lower sampling mesh size was 10 µm. MP samples were collected ca. 1–3 m away from the river shore at the sampling sites during daylight for all four sampling campaigns in the surface water (upper 0.1–0.3 m) using an *in-situ* cascade filtration pump [Universal Filtration Object (UFO) developed by Aalborg University, (Rist et al., 2020), Supplementary Figure S1]. The same sampling approach was used by Sefiloglu et al. (2024) to determine microplastic concentrations in Amsterdam surface waters. Seven liters per minute of water were pumped through a 5,000 µm grid cage and stainless-steel tube over stainless steel filters of first 300 µm and then 10 µm pore-size. One sample consisted of four filters (16 cm in diameter and 10 µm pore size). A pressure threshold of 1.8 bar indicated filter clogging. Sampling volumes vary from 74L to 940L depending on the water conditions as higher suspended particulate matter in the water led to faster clogging.

The loaded filters were rinsed and ultrasonicated (2–4 min) before hydrogen peroxide (10 vol% H_2O_2) wet oxidation for 18–24 h at 30°C, and the solution was filtered afterwards. This was followed by sodium-iodide (density 1.63–1.7 g cm^{-3} NaI) density separation using JAMSS density separator units (Nakajima et al., 2019) and volume-reducing "anodisc" (0.2 µm, Whatman) filtration. During the procedures, the filters were stored in clean glass Petri dishes at room temperature. After oxidation and density separation, the filters were rinsed and ultrasonicated. The extracted particles on the anodisc filters were then analyzed by micro-Fourier transform infrared spectroscopy (µ-FTIR, Supplementary Material S2) with a detection limit (pixel resolution) of 25 µm. Spectra were further interpreted using systematic identification of MP in the environment (siMPle®) software [Supplementary Material S3, Primpke et al. (2020)] providing characteristics such as polymer type, particle dimensions, and mass (calculated by the software using minor and major dimension, particle thickness estimated at 0.6 × 2 × minor dimension, polymer density, and assuming an ellipsoid shape). The sample processing is visualized in Supplementary Material S4.

Throughout the study, strict protocols were followed to ensure the integrity of the samples and prevent MP contamination. To minimize the risk of synthetic material contamination, all personnel always wore cotton lab coats and refrained from wearing synthetic clothing. All procedures were executed under a laminar flow bench or fume hood. All solutions used were pre-filtered (GF/D 2.7µm, Whatman). Glassware, glass-fiber, and stainless-steel filters were muffled, i.e., temperature treatment at 500°C for 2–3 h. Workspaces were routinely cleaned. Plastic materials were avoided during laboratory processes except for sample processing for campaigns July 2021 and November 2021, where polyethylene (PE) squeezing bottles with polypropylene (PP) caps were utilized for rinsing. Procedural blanks (~100 mL of filtered tab water) were carried out in parallel to the sample processing as of the H_2O_2 oxidation for MPs (results see Supplementary Material).

2.1.2.2 Physical water quality parameters

Temperature, pH, and conductivity were measured during each MP sampling campaign using a multiprobe (Multiline P4, WTW). A clean stainless-steel bucket was filled with >5L of river surface water, and measurements were taken inside the bucket. Turbidity was measured as nephelometric turbidity units (NTU) in triplicate using an *in-situ* turbidity meter (Hach 2100P Turbidimeter). Suspended sediment concentration (SSC) was determined from a 1-L sample of river water following the standard procedure ASTM D3977 with a slight modification of drying temperature (>48 h at 60°C). The total sample was filtered on a muffled GF/F filter (pore size 0.7 µm, Whatman), dried and weighted.

2.1.2.3 Hydrological data

For each sampling site, the distance from the river source and the river catchment area up to that point are obtained from HydroSHEDS data (Lehner and Grill, 2013).

Data of river discharge (Q, m^3s^{-1}) and water level (H, m) for the Seine and Marne Rivers and relevant tributaries near the confluences were obtained from 18 hydrological monitoring stations as daily averaged values from the Central Service for Hydrometeorology and Support for Flood Forecasting in France (Hydro Eaufrance, 2023).

Flow velocity (five replicates, m s^{-1}) was measured in the surface water during MP sampling with a portable flowmeter (Flo-mate Model 2000; Marsh-McBirney Inc.). Measurements were not

always possible or reliable due to challenging conditions, especially low water flow close to the shore, and the limitation of the instruments' accuracy [±2% plus zero stability (1.5 m s^{-1})].

Daily precipitation data were obtained from Prevision-Meteo (2023) for three weather stations for the months of the sampling campaigns. Data from station Paris-Montsouris, located in central Paris, were used for sampling sites M1, S2, S3, S4, and S5. Precipitation data from Paris Melun-Villaroche and Evreux-Fauville were related to sampling sites S1 and S6, respectively.

2.1.2.4 Data on sewage discharges as microplastic sources

The acquired data include locations and daily discharge volumes for five selected WWTP effluent locations and twelve of 38 CSO outfall locations, each holding >1% of discharge and together presenting 91% of the CSO volumes discharged during the monitoring period (Figures 1B, C). Data were provided by SIAAP. The CSO outfall sites Clichy and La Briche are located downstream of sampling site S3, holding 31% and 25%, respectively.

Four large WWTPs are located along the Seine in the Paris urban area. Notably, the WWTP Paris Seine-Amont (SAM) is located a few kilometers before sampling site S2, while the WWTP Seine-Centre (SEC) is upstream of site S4. WWTPs Seine-Aval (SAV) and Seine Grésillons (SEG) are between S4 and S5. WWTP Marne Aval (MAV) is in the Marne River and related to sampling site M1.

2.2 Data analysis

We used the free software for statistical computing R (version 4.3.0) to conduct the data analyses (R Core Team, 2021). A Non-parametric Spearman rank test was applied to assess correlations between variables. Replicates of physical water parameters were averaged. For *MP summary* (Supplementary Material) MP (mass) concentrations and fluxes were reported as a sum of all individual particles per sample. MP polymer type proportions and sizes per campaign were weighted by sample size.

2.2.1 Microplastic data

MP data exploration followed the protocol outlined by Zuur et al. (2010). Some particles with major dimension above 300 µm (6.2%) went through the filter during sampling. For comparability, MP particles from 25 to 300 µm were analyzed. The size limits were chosen to focus on smaller MP with comparability to other studies (Dris et al., 2024).

MP numeric (further on referred to as MP concentration) and mass concentrations (Eqs 1, 2) were calculated as the number of observations (N) or particle mass divided by the sampling volume (V_S) of the respective sample and converted into number of particles m^{-3} and ngL^{-1}. The concentrations were estimated for different groups, e.g., per campaign and sampling site, and polymer type.

$$\boldsymbol{MP\ concentration}\ [\boldsymbol{particles\ m^{-3}}] = \frac{\mathbf{N}\ [\boldsymbol{particles}]}{\boldsymbol{V_S}\ [\boldsymbol{m^3}]} \quad (1)$$

$$\boldsymbol{MP\ mass\ concentration}\ \ [\boldsymbol{ng}\ \mathbf{L^{-1}}] = \frac{\mathbf{mass}}{\boldsymbol{V_S}\ [\mathbf{L}]} \quad (2)$$

The MP (mass) flux (Eqs 3, 4) was calculated as MP (mass) concentration multiplied by the river discharge (Q) per sampling event as particles s^{-1} or mg s^{-1}.

$$\boldsymbol{MP\ flux}\ [\boldsymbol{particles\ s^{-1}}] = \boldsymbol{MP\ concentration}\ [\boldsymbol{particles\ m^{-3}}] * \boldsymbol{Q}\ [\boldsymbol{m^3 s^{-1}}] \quad (3)$$

$$\boldsymbol{MP}\ \mathbf{mass}\ \boldsymbol{flux}\ [\mu \boldsymbol{g s^{-1}}] = \boldsymbol{MP\ mass\ concentration}\ [\mu \boldsymbol{g\ m^{-3}}] * \boldsymbol{Q}\ [\boldsymbol{m^3 s^{-1}}] \quad (4)$$

2.2.2 Water balance

For the 1-year monitoring period (with sampling durations of about 2 weeks per campaign) a water balance (Supplementary Material S5) of the Seine River discharge was conducted to quantify the hydrodynamic conditions and to study MP transport and fate. Balances were generated for the hydrological stations in the Seine. Discharge data of the Seine and tributaries were considered. The balances were calculated as the differences between the inflows and outflows. The downstream discharge Q_x (Eq. 5) is the sum of the previous upstream discharge (Q_0) and the incoming tributary discharges (Q_i) between Q_0 and Q_x. Acknowledging that ground water flow into the river and evaporation are to be assumed negligible with respect to the discharge, the difference (Eq. 6) should be close to 0 $m^3 s^{-1}$.

$$\mathbf{Q_x} = \mathbf{Q_0} + \sum \mathbf{Q_i} \quad (5)$$

$$\boldsymbol{Difference} = \boldsymbol{Q_x} - \boldsymbol{Q_0} - \sum \boldsymbol{Q_i} \stackrel{\text{def}}{=} \mathbf{0} \quad (6)$$

3 Description of the data and initial analyses

3.1 Microplastics

The dataset contains comprehensive data of individual MP particles (total N = 5,922) per sampling site and sampling day, detailing particle characteristics (mass, polymer type, minor, major, and ferret dimension). For number and mass, MP concentrations and MP fluxes were estimated for each campaign per sampling date, and sampling site (Figures 2B, C; Supplementary Material *MP summary*). The median MP concentration was ~600 particles m^{-3} and MP flux 165 × 10^3 particles s^{-1}. MP mass concentrations and mass fluxes ranged between 2 and 960 µg m^{-3}, and 57 and 500 × 10^3 µg s^{-1}, respectively. The annual estimated MP concentration and MP mass flux in the Seine are 5.19 × 10^{12} particles yr^{-1} and 0.816 t yr^{-1}, respectively.

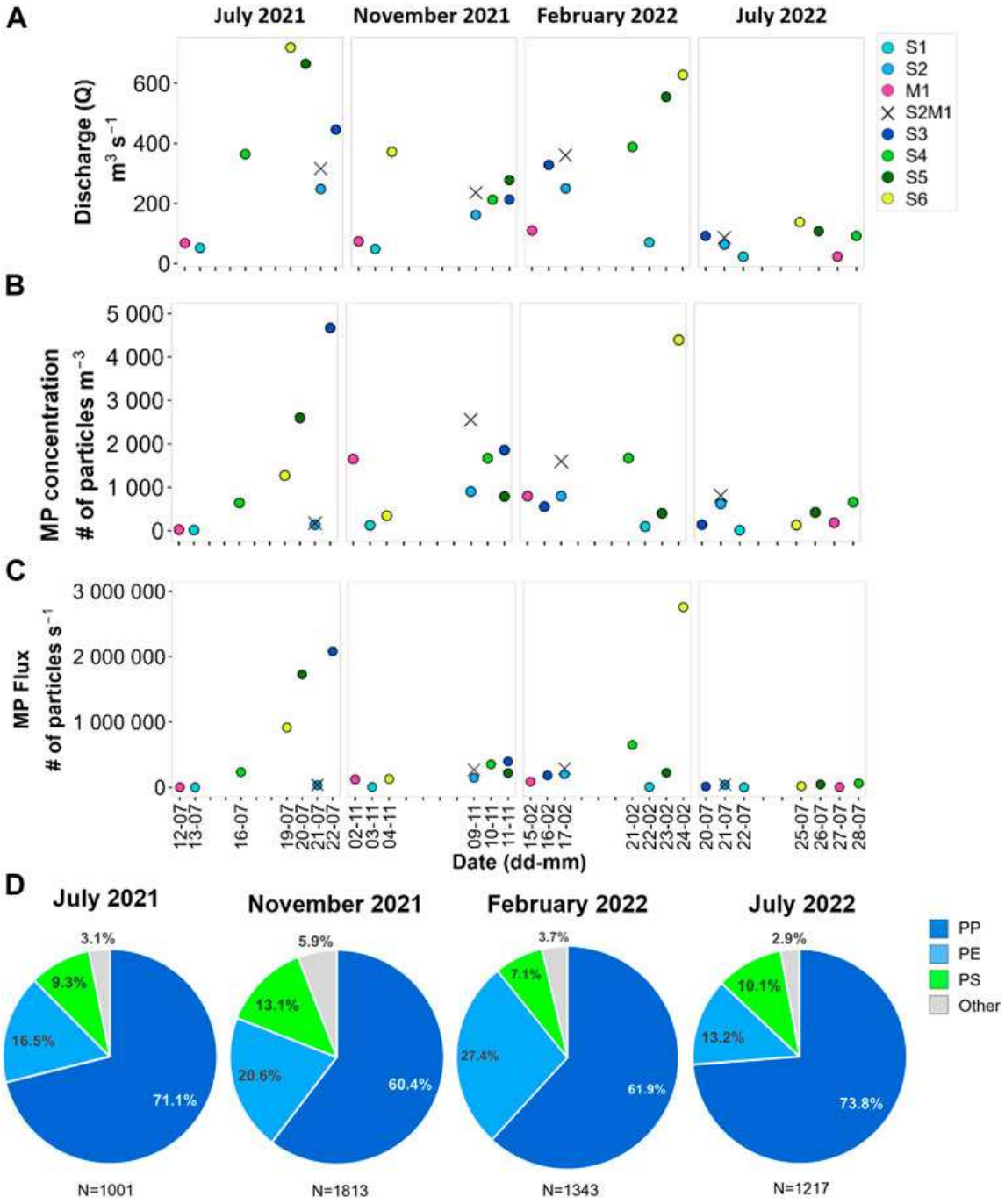

Figure 2. Graphs **(A–C)** show data on River discharge, microplastic (MP) concentration, and MP flux, respectively, along the period (x-axis, date indicating day-month) of the four sampling campaigns (panel headings) for each sampling site (legend), # indicating number. Because site M1 presents a potential MP contribution from the Marne River into the Seine River, we have combined the values from sites S2 and M1 (S2M1) to enhance comparability with the subsequent downstream site S3. **(D)** Pie charts of the proportions per sampling campaign based on numeric concentration of polypropylene (PP), polyethylene (PE), polystyrene (PS), and all other detected polymer types. N = Number of particles per campaign, sampling site M1 was excluded.

MP concentrations varied across sampling sites and campaigns between 14 particles m^{-3} (S1) and 4,700 particles m^{-3} (S3). MP fluxes ranged from 300 particles s^{-1} (S1) to 2.67 × 10^6 particles s^{-1} (S6). For each campaign, the lowest MP concentrations were always found at the upstream

sampling site S1. The MP fluxes for S1 (ranging from 300 to 6,000 particles s^{-1}) are smaller than the MP flux values of sampling sites S2–S6 (ranging between 13 × 10^3 and 2.76 × 10^6 particles s^{-1}), with a median of 165 × 10^3 particles s^{-1}. MP concentration correlates moderately (ρ = 0.65, p < 0.01) to river discharge, MP (mass) flux (ρ = 0.89, p<0.01; ρ = 0.85, p < 0.01) correlates stronger to river discharge.

The MP concentrations in the Seine are comparable to higher concentrations reported in European rivers' surface water (Gao et al., 2023).

Sixteen polymer types were identified including acrylics, epoxy and rubber (Supplementary Material S5), and the most abundant polymer types across all Seine samples were polypropylene (PP) (concentration: 67%, mass concentration: 48%), polyethylene (PE) (19%, 38%), and polystyrene (PS) (10%, 10%), reflecting similar findings in European rivers (Scherer et al., 2020; Gao et al., 2023; Sefiloglu et al., 2024). The polymer type distribution is relatively consistent across the four campaigns (Figure 2D) and similar across sampling sites with deviations observed for some individual samples (Supplementary Material S5). The median MP particle minor and major dimensions overall were 53 µm and 96 µm (Supplementary Material S6). Smaller MPs consistently exhibited higher MP concentrations and fluxes across all samples. PE particles are found to be larger than PS and PP (PP exhibits the smallest major dimensions overall).

3.2 Physical water quality parameters

Suspended sediment concentration (SSC) ranged from 0.5 mg L^{-1} (S1) to 51.7 mg L^{-1} (S3). Turbidity values ranged from 2.6 to 23.7 NTU, pH was between 7.5 and 8.3, and water temperatures ranged from 7°C to 26°C. Spearman correlation tests resulted in turbidity and SSC, as expected due to collinearity, being correlated (ρ = 0.77, p < 0.05). Turbidity correlated with MP concentration (ρ = 0.50, p < 0.05) and flux (ρ = 0.64, p < 0.05).

3.3 Hydrological conditions

The flow regimes during the monitoring did not conform to the habitual low flows during summer and high flows during winter. High precipitation in July 2021 in Western Europe influenced the summer flow in the Seine. On the contrary, fall has been dry leading to low flows. We captured different river discharge conditions ranging from 23 to 719 m^3s^{-1} (Figure 2A). River discharges on sampling days across all Seine sampling sites (S1-S6) were higher during the July 2021 and February 2022 campaigns (range, median: 52–719, 364 m^3s^{-1}; and 70–628, 328 m^3s^{-1}, respectively), but lower in November 2021 (48–327, 212 m^3s^{-1}), and lowest during July 2022 (23–138, 92 m^3s^{-1}). The dataset contains the river discharge for each relevant sampling.

Water balances are important for evaluating MP flux and concentration observations. Fluctuations in river discharge and deviations in the water balances can be used to understand MP dynamics. For example, the MP concentration in the Seine River may be elevated due to tributary contribution, sewage overflow and runoff during peak discharge. Five water balance calculations with daily river discharge data were conducted (Supplementary Material S7). As a result of the discharge differences, the balances show deviations around normal levels (up to ~10%). Discharge data per hydrostation are included in the Supplementary Material (*Water-balance*).

We collected precipitation data concerning the monitoring period (from 2 weeks before the start of a sampling campaign until the end) to later assess its influence on the river flow dynamics and

MP concentration. Precipitation can lead to increased river discharge, turbulence, CSOs, and surface runoff, potentially transporting MPs into rivers.

3.4 Sewage discharges

Between 1 July 2021, and 1 August 2022, WWTP effluent daily discharge volumes (Supplementary Material *WWTP discharges*) range from around 150 × 10^3–1 × 10^6 m^3 day^{-1} (SAM), 1 × 10^6–3.4 × 10^6 m^3 day^{-1} (SAV), up to 500 × 10^3 m^3 day^{-1} (SEC), 30 × 10^3–325 × 10^3 m^3 day^{-1} (SEG), and 14 × 10^3–100 × 10^3 m^3 day^{-1} (MAV).

Up to 47 CSOs happened during the 1-year monitoring period. Several CSOs were recorded just before and during the sampling campaign in July 2021, and one CSO event before the campaign in November 2021 for CSO outfall sites La Briche and Clichy (Supplementary Material *CSO discharges*). The maximum daily discharge volumes during the monitoring periods occurred on 13 July 2021, and were 945 × 10^3 m^3 (Clichy) and 963 × 10^3 m^3 (La Briche). Other CSO outfall sites contribute significantly to the annual CSO discharge.

4 Conclusion and potential uses of this dataset

This dataset presents comprehensive data of MP contamination in the Seine River and various environmental and hydrological conditions. Preliminary results show that MP levels are locally highly variable which may be attributed to hydrological conditions. This report facilitates the calculation of MP contamination metrics, analysis of relationships with environmental and hydrological variables, and the assessment of the environmental impact. The knowledge derived from analyses offers insights for research, modelling, environmental education, and policy of MP pollution in rivers. The dataset can be augmented with future data.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found below: https://zenodo.org/records/10658366?token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6IjFiMGY2ZGNiLTcyYWUtNGNmOC05ZmNhLWZhZDZmN2FlMTBmNSIsImRhdGEiOnt9LCJyYW5kb20iOiI2NWUyNzk2Y2U3YWVhNmMxMWZkNGRkMjZlMTE2YjJiZSJ9.32rBjQV
o7DJShBEGzbdlzurmySXmwDPYTnNiCLOQSniiEm7y5ohgmAB5lxIR1gbFUwX_iORsbxZB-fvXQrJzg, Zenodo LimnoPlast.

Author contributions

CS: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Project administration, Visualization, Writing–original draft, Writing–review and editing. RD: Conceptualization, Writing–review and editing, Funding acquisition, Investigation, Methodology, Supervision, Project administration. JG: Conceptualization, Funding acquisition, Methodology, Supervision, Writing–review and editing. FB: Formal Analysis, Methodology, Supervision, Writing–review and editing. AM: Formal Analysis, Methodology, Supervision, Writing–review and editing. SG: Resources, Writing–review and editing. AV: Methodology, Supervision, Writing–review and editing. BT: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2024.1386547/full#supplementary-material

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Uwe Schneidewind, University of Birmingham, United Kingdom

Reviewed by:

Reza Dehbandi, University of Birmingham, United Kingdom
Mohammad Wazne, Université Claude Bernard Lyon 1, France

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***Correspondence:** Cleo N. Stratmann, c.stratmann@posteo.de; Rachid Dris, rachid.dris@u-pec.fr

[†]Deceased

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CHAPTER 4 DYNAMICS AND FATE OF MICROPLASTIC IN THE SEINE RIVER IN THE GREATER PARIS AREA (PAPER II)

Manuscript to be submitted to Frontiers in Earth Science – Hydrosphere as a contribution to the research topic 'Microplastic and Nanoplastic Fate and Transport in Groundwater, Surface Water, and Soil Ecosystems: Occurrence, Methods, and Perspective' (Summary accepted, planned submission in November 2025), Article type: Original research

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Dynamics and Fate of Microplastics in the Seine River in the Greater Paris Area

Cleo N. Stratmann[1]*, Rachid Dris[1]*, Johnny Gasperi[2], Frans A. Buschman[3], Arjen A. Markus[3], Sabrina Guerin[4], A. Dick Vethaak[3,5,†], Bruno Tassin[1]

[1]LEESU, ENPC, Institut Polytechnique de Paris, Univ Paris Est Creteil, Marne-la-Vallée, France

[2]Laboratoire Eau et Environnement GERS-LEE, Université Gustave Eiffel, France

[3]Deltares, Delft, The Netherlands

[4]Syndicat Interdépartemental pour l'Assainissement de l'Agglomération Parisienne (SIAAP), France

[5]Amsterdam Institute for Life and Environment (A-LIFE), Vrije Universiteit Amsterdam, Amsterdam, The Netherlands

[†]Dick Vethaak sadly passed away in 2024.

*** Correspondence:**
Cleo N. Stratmann (C.stratmann@posteo.de), Rachid Dris (rachid.dris@u-pec.fr)

Keywords: Microplastic Fluxes, River hydrology, Urban plastic pollution, Sewer discharges, Water pollution, Hydrometeorological variables

Abstract

Research studies globally have confirmed the presence of microplastics (MPs) in rivers. Urban rivers have received special attention due to the abundance of human activity and MP-emitting sources, such as sewer effluents. Over the past decade, researchers have reported elevated levels of MPs in the Seine River in France, with high temporal and spatial variations. This study investigated the fate and dynamics of small MPs [25-300 µm] in the Seine River around Greater Paris under low (23 m^3 s^{-1}) to high (719 m^3 s^{-1}) flow conditions, as well as along the urban gradient, during four campaigns between 2021 and 2022. Six sites, ranging from upstream (Marnay-sur-Seine) to downstream (Poses), exhibited MP concentrations ranging from 14 to 4,700 particles m^{-3} (mass concentrations ranging from 2 to 962 µg m^{-3}), with higher levels observed during periods of high river discharge and in urban and downstream areas. MP concentrations and number of polymer types (maximum of 13 polymers per site) tend to increase towards urban and downstream sites, but the particle sizes distribution was homogeneous overall (median: 80 µm) and dominated by polypropylene (PP), polyethylene (PE) and polystyrene (PS). MP fluxes increased up to 70-fold from upstream to the urban center with loads in Paris center of up to 1.3 t y^{-1}. The MP load in the downstream area was periodically higher (median 3.6 t y^{-1}) due to high MP concentrations and river discharge in February 2022. However, load was 30% lower during the other three campaigns, suggesting that MPs in the upper water layer could potentially accumulate in urban areas of the Seine. The MP mass balance clearly indicates MP inputs or mobilization of MPs from the urban area and retention or accumulation in the urban center and downstream areas. Precipitation-driven wastewater treatment plant (WWTP) effluent and combined sewer overflows (CSOs) were correlated with a noticeable increase in MP concentration and load at multiple sampling sites in the following days. The high MP variations and heterogeneous dynamics demand further research.

Highlights

- MP concentrations were lowest upstream of Paris, increased toward urban areas and downstream, and varied strongly over time, especially under high-flow conditions
- PP, PE, and PS dominated polymer composition of in total sixteen polymer types several polymer types increased in concentration towards urban sites, Some polymer types (e.g., acrylic, cellulose acetate) occurred only occasionally.
- MP sizes were consistent across samples, indicating a homogeneous “MP soup,” with PE tending to be larger and PP smaller.
- River flow and rainfall influenced MP concentrations, with peaks linked to increased WWTP effluent and CSO discharge.
- Rainfall facilitated increased WWTP effluence and CSO resulting in increased MP abundance
- The MP mass balance indicates MP accumulation/retention in the river with periodical downstream transport linked to higher river flow

1 Introduction

Microplastics (MPs) are plastic particles smaller than 5 mm either produced in small size (primary MPs) or fragmented from larger plastics (secondary MPs). They are a major component of global plastic pollution in the environment, with diverse impacts on organisms and ecosystems through their persistence, mobility, potential for bioaccumulation and toxicity, e.g., ability to accumulate and release harmful chemicals (Lambert & Wagner, 2018; Wagner et al., 2024). Rivers impacted by urban and agricultural areas are particularly susceptible to MP pollution due to increased anthropogenic activity and an aggregation of MP sources (Kunz et al., 2023; Lambert & Wagner, 2018). Many studies investigated MP concentrations in rivers (A Azizi et al., 2022; Birch et al., 2020; Lechner et al., 2014; Sefiloglu et al., 2024; Vidal et al., 2023) including shedding light on sources such as surface runoff or urban wastewater or focused on modelling MPs transport dynamics (Al-Zawaidah et al., 2024; Besseling et al., 2017; Bondelind et al., 2020; Domercq et al., 2022). However, the fate of riverine MPs and the influence of changing hydrometeorological and environmental conditions *in-situ* has been studied less (de Carvalho et al., 2021; Kukkola et al., 2023; Treilles et al., 2021, 2022; Wei et al., 2022). Field studies are cumbersome and may be limited in terms of controlling input variables and or biases, but it is the ultimate way to understand environmentally relevant MPs and their fate in rivers and urban areas with all the complex influences they are exposed to (Koelmans et al., 2022).

The Seine River in France (average discharge in Paris Austerlitz: 350 m3 s-1) is significantly influenced by population density and anthropogenic activities, including urban development, industrial operations, and agriculture, as it flows through the Greater Paris urban agglomeration (Île-de-France) with over 12 million inhabitants and increasing (Tabuchi et al., 2016). The water quality of the Seine recovered in the past half century due to better sewage and stormwater treatment, but the river is still under environmental pressures. Those include sewage inflows, shipping, pollutants including MPs, and climate change causing more extreme hydrometeorological conditions, especially lower flow rates (Tabuchi et al., 2018).

Sources of MPs to rivers are manifold and include littering, wind transport, atmospheric deposition, stormwater and surface runoff, ship paints, urban wastewaters, i.e., wastewater treatment plant (WWTP) effluents and during intense precipitation combined sewer overflows (CSOs) (Dris et al., 2016; McCormick et al., 2016; Nguyen et al., 2024; Österlund et al., 2023; Treilles et al., 2021). Paris has 2,100 km of combined sewer system and heavy rain often leads

to CSOs (SIAAP, 2023). Recently, Nguyen et al. (2024) investigated MP in the Parisian sewer pipes and suspect that CSOs contribute strongly to MP contamination in the Seine River. MPs in the Seine River were investigated since ~2015. In one of the first studies from Dris et al. (2015) MP >100 µm were sampled in the water surface using nets and concentrations were estimated between 4 - 108 particles m^{-3} varying across locations and seasons. Following studies used similar sampling techniques (trawls, nets) showing that rainfall increased (variation of) microfiber deposition and that urban sites received higher amounts (Treilles et al., 2021). Later on, Treilles et al. (2022) investigated downstream versus upstream MPs and concluded that neither river discharge nor urbanization significantly influence MP concentrations, sizes or polymer types, but that MP mass fluxes increased with urbanization. Comparisons of MP concentrations in flood versus non-flood conditions showed that MP concentrations were higher in low flow conditions. Further research on MP dynamics under different conditions and in more locations in the Seine is needed.

The size of MP particles is an important parameter when assessing MPs fate and environmental impact in rivers (Besseling et al., 2017; Castro-Castellon et al., 2022; Kooi & Koelmans, 2019; Scherer, Wolf, et al., 2020; Wagner & Lambert, 2018). Limitations in sampling techniques meant previous studies typically focused on larger particles (>80 µm or >300 µm; Dris et al., 2015; Treilles et al., 2018). With methodological advances it is now possible to sample and analyze smaller MPs (Dris et al., 2024). Due to fragmentation, smaller particles are estimated to be more ubiquitous (Chamas et al., 2020; Thompson et al., 2024) and the small size allows them to be more easily transported and absorbed by living organisms. We investigated MPs with particle dimensions between 25-300 µm, a size range with bioavailability to aquatic organisms (Wagner & Lambert, 2018). Due to their similar size microplastics (MPs) are suspected to behave similar to suspended solids, and correlations between suspended sediment concentrations (SSCs) and riverine MP concentrations have been observed, particularly during flood events (Mohsen et al., 2023). Certain grain fractions (e.g. fine sand) have been linked to microplastics (MPs) of comparable size and density (Enders et al., 2019). As SSC is influenced by hydrodynamic conditions and material availability, it can provide insights into microplastic dynamics, such as dispersion, deposition, and resuspension. Given the risks that MPs pose to aquatic ecosystems and the need for improved water quality in the Seine, more relevant field data is crucial. Understanding the concentrations and dynamics of MP helps to identify transport pathways, as well as potential ecological risks.

This study investigates the occurrence and dynamics of small microplastics (25 – 300 µm) in the upper water column (depths of 0.1 – 0.5 m) of the Seine River, focusing on the Greater Paris area. The study aims to improve our understanding of the abundance, composition, and potential sources of these particles, particularly in relation to urban drainage infrastructure and hydrometeorological conditions. The following research questions guide the analysis: How do microplastic concentrations and fluxes vary in space and time in the Seine River? What are the typical polymer types and size distributions of microplastics across the river system? Can hydrometeorological conditions and urbanization explain MP levels? What role do urban sewer infrastructures (i.e., WWTP effluent outlets and CSOs) play for riverine MP abundance? To address these questions, we analyzed data from a field study: MP samples were collected along the Seine River upstream and downstream of Paris over the course of one year (July 2021–July 2022). The sampling area included a reference site located well upstream of the urban zone, four urban sites, and a downstream site located before the estuary. Results from this study help clarify how MP concentrations relate to hydrometeorological conditions and urban infrastructure,

providing a basis for targeted future research and contributing to the development of effective mitigation strategies for the Seine River and other urban waterways.

2 Materials and Methods

This current study builds upon the previously published dataset on a one-year microplastic (MP) field survey in the surface water of the Seine River in Northern France between 2021-2022 (Stratmann et al., 2024). The dataset includes MP contamination metrics (concentration, flux, mass flux) and individual particle characteristics (polymer types, particle dimensions and volumes), hydrometeorological conditions, water quality parameters, and urban wastewater discharge volumes. In addition to the dataset, the above-mentioned publication details the study design and materials and methods, which are also briefly summarized below.

2.1 Study site

The field study was conducted on the French Seine River (750 km long) extending upstream and downstream of Greater Paris (Figure 1). Greater Paris (inside Île-de-France) supplies a large part of the French GPD and gathers ~9 M inhabitants (Joint Research Centre, 2015), causing a major impact on the river. The river is subjected to global industry impacts, including heavy ship traffic, industry activities, water extraction, and agriculture. The mean annual discharge is 310 $m^3 s^{-1}$. in Paris center (Tabuchi et al., 2018) and increases to 611 $m^3 s^{-1}$ downstream (Poses). The distinct flow seasons are summer-autumn (low, 5-year average monthly flow: 82 $m^3 s^{-1}$) and winter, high with peaks in February (5-year average monthly flow: 1,400 $m^3 s^{-1}$), driven by precipitation. In addition, four reservoirs located in the upper part of the catchment help to maintain the flow over 100 $m^3 s^{-1}$ in summer and to limit high flow during flood events (Flipo et al., 2021; Tabuchi et al., 2015). Six sampling sites were selected at the Seine and one at the Marne tributary. The sampling locations covered 442 km along the river from up- to downstream of Greater Paris. The sites varied in their river morphology rural to highly urbanized, often with concrete vertical bank infrastructure, bridges and locks and were categorized as rural upstream (S1), urban (S2 – S5) and rural downstream (S6). Within the urban area, four wastewater treatment plants (WWTPs) and multiple combined sewer overflow (CSO) locations (Figure 2) influence the river (Tabuchi et al., 2018). Average WWTP effluent discharge is around 800 Mm^3 annually (SIAAP, 2023). Two CSO locations (Clichy and La Briche) are the most important ones and are situated in the center of Paris.

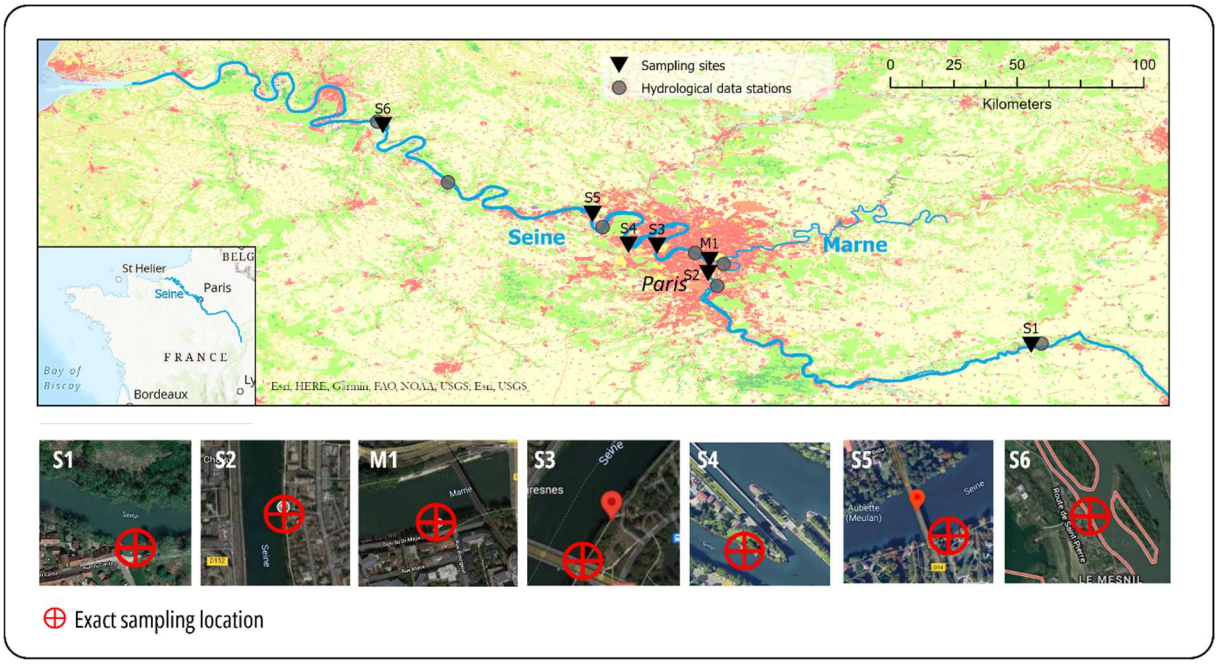


Figure 1 Monitoring area around Greater Paris with Seine sampling sites S1 (rural upstream), S2-S5 (urban), S6 (rural downstream) and Marne Rvier sampling site M1; S1 = Marnay-sur-Seine, S2 = Choisy-le-Roi, M1 = Marne à Alfortville, S3 = Suresnes, S4 = Bougival, S5 = Triel-sur-Seine, S6 = Poses; hydrological data stations provided river discharge data. Bird-view pictures were modified from Google maps.

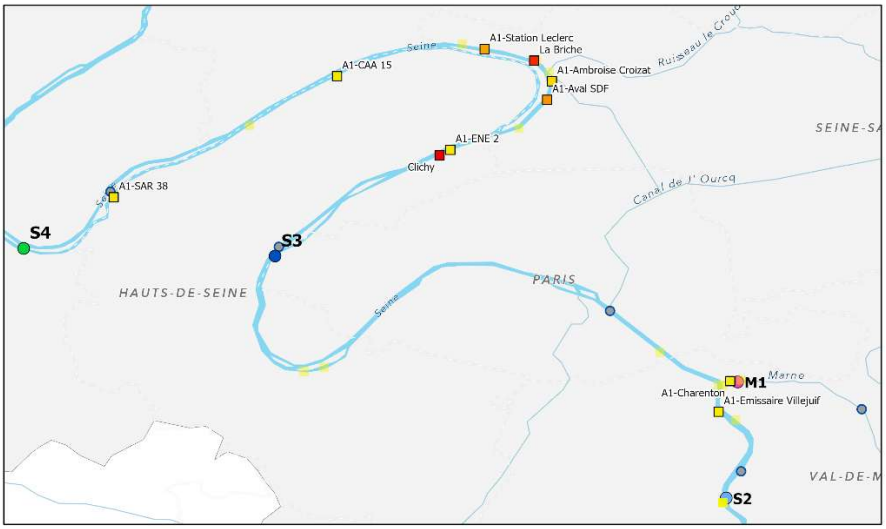


Figure 2 Combined sewer overflow (CSO) outfall locations (squares) around Paris in the monitoring area S2-S4, M1 are sampling sites, Color code for CSO: yellow = low discharge, red = high discharge.

2.2 Sampling and sample processing

The field study included two sampling campaigns conducted in summer low flow (LF) conditions in July 2021 (Jul-2021) and July 2022 (Jul-2022); and two campaigns in winter with

high flow (HF) conditions: in November 2021 (Nov-2021) and February 2022 (Feb-2022) (Table 1). Sampling campaign duration varied between 7 and 10 days. For practical reasons, the order of sampling did not follow an upstream downstream order and varied from one campaign to another. For MP analysis, water samples up to ~1 m^3 (range: 73 – 940 L) were collected from the upper water column, but not the water surface directly. Samples were taken ca. 1,5 m from the river bank with plastic-free *in-situ* filtration-pump equipment [Universal Filtration Object (UFO) developed by Aalborg University, (Rist et al., 2020)]. A filtration cascade was integrated in the pump with first 300µm and then 10µm stainless steel mesh. In the laboratory, samples underwent wet oxidation with hydrogen peroxide, density separation with sodium iodide solution (density >1.6), and several filtration steps before spectrometric µFTIR analysis and software-based particle characterization with siMPle® version 1.1.β (Primpke, S. et al., 2019). The software automatically calculated particle masses based on the software-own algorithm. MPs between particle dimension of 25-300 µm with the lower size limit determined by the µFTIR spectral resolution of 25µm per pixel were analysed. In addition, physical water quality parameters (turbidity, suspended solid concentration (SSC), temperature, conductivity) were assessed at each sampling site. Continuous river discharge data were collected from multiple hydrological stations (Hydro Eaufrance, 2023) within the monitoring area. Data on WWTP effluent on CSO discharge were obtained for the period of the samplings from SIAAP. These data are essential for contextualizing MP concentrations within the broader environmental and urban conditions.

Table 1 Microplastic sampling sites and dates of sampling per campaign; color gradient from bright to dark represents timeline from earliest to latest sampling date per campaign.

	Sampling campaigns (Month Year)			
	July 2021	November 2021	February 2022	July 2022
Sampling sites	**Sampling dates (dd-mm-YYYY)**			
S1 Marnay-sur-Seine	13-07-2021	3-11-2021	22-02-2022	22-07-2022
S2 Choisy-le-Roi	21-07-2021	9-11-2021	17-02-2022	21-07-2022
M1 Marne à Alfortville	*12-07-2021*	*2-11-2021*	*15-02-2022*	*27-07-2022*
S3 Suresnes	22-07-2021	11-11-2021	16-02-2022	20-07-2022
S4 Bougival	16-07-2021	10-11-2021	21-02-2022	28-07-2022
S5 Triel-sur-Seine	20-07-2021	11-11-2021	23-02-2022	26-07-2022
S6 Poses	19-07-2021	4-11-2021	24-02-2022	25-07-2022

2.3 Data analysis

Exploratory data analysis, non-parametric statistical testing, and correlation and regression analysis were employed, using R version v.4.3.3 (R Core Team, 2021) and statistical packages (Patil, I., 2021). This approach is well suited to our dataset, which includes small sample sizes and non-normal distributions. We applied the Spearman rank test to assess the direction and strength of correlations between variables. In this study, the non-parametric, pairwise Kruskal-Wallis test was used to analyze differences in the response variables between groups, with significance calculated using Dunn's method. Based on the recommendation of Hartmann et

al. (2019) the MP size assessment was based on the major particle diameter (further referred to as *size*), which is the most relevant dimension in terms of bioavailability and toxicity from an ecological perspective.

A MP mass flux balance was introduced to quantify the transport, input, (de)mobilization and/or retention of MPs between sampling sites along the Seine. Per campaign, we calculated the difference of MP mass fluxes (Δ MP mass flux), also described as mass load, between consecutive sampling sites (S_i, S_{i+1}) (Eq. 1). A positive difference indicated input or mobilization of MPs and a negative difference signaled MP retention or mobilization (sink'). No change suggested that the mass of MP transported through the river cross section is constant.

$$MP\ mass\ flux\ S_{i+1} = MP\ mass\ flux\ S_i + \ \Delta\ MP\ mass\ flux \qquad \text{(Eq. 1)}$$

For site S3, the equation is slightly modified (Eq. 2) as the mass balance includes inflow from the Marne River (site M1):

$$MP\ mass\ flux\ S_3 = MP\ mass\ flux\ S_2 + \ MP\ mass\ flux\ M_1 + \Delta\ MP\ mass\ flux \quad \text{(Eq. 2)}$$

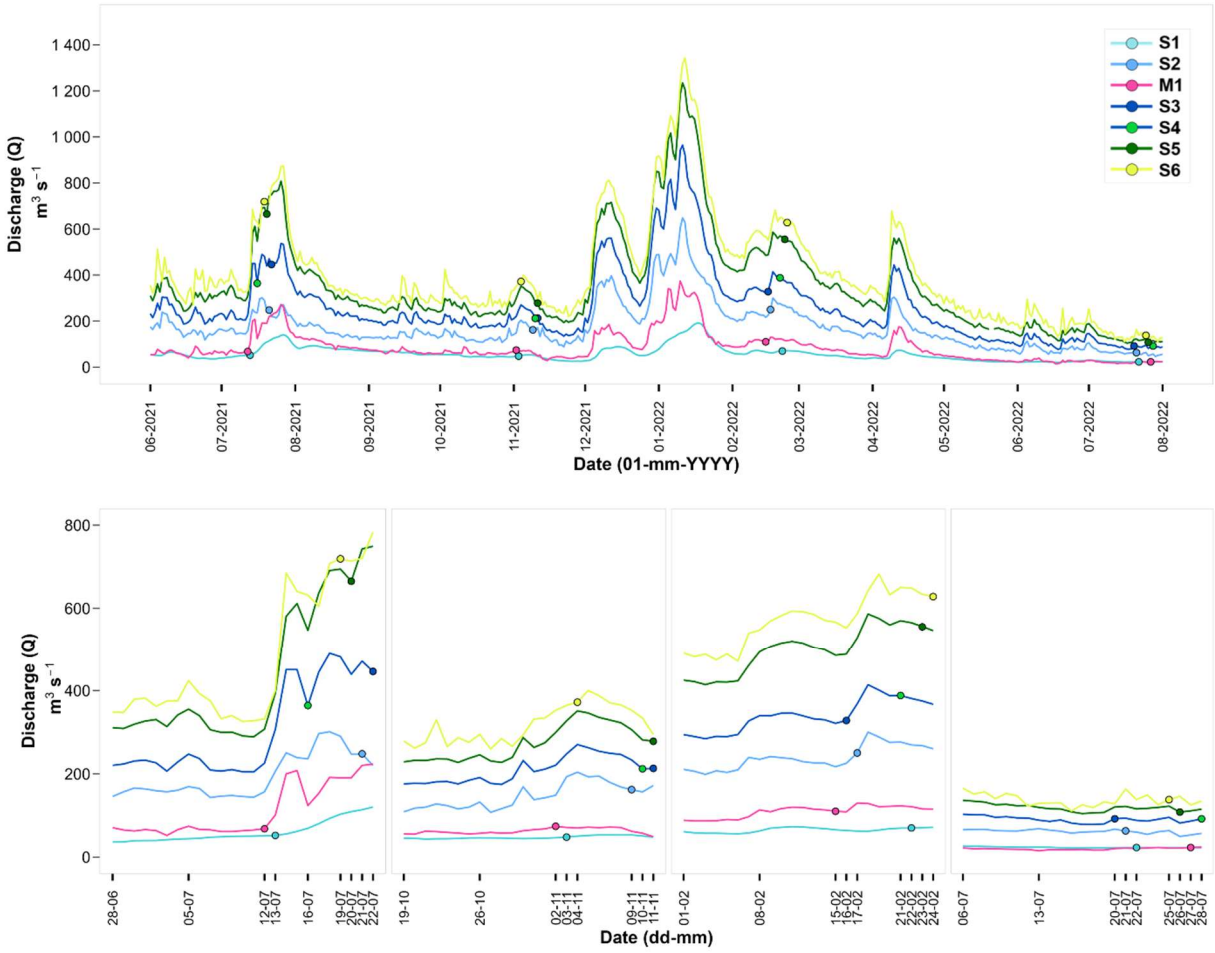
The mass flux balances were visualized for each campaign using Sankey diagrams made with RAWGraphs (Mauri et al. 2017, version 2.0). In addition, we created radar plots using RAWGraphs version 2.0 (Mauri et al., 2017) visualizing the complex dynamics between river discharge, MP concentrations and MP fluxes across sampling sites. To enable comparison of the dynamic patterns between sites, variables were normalized to their respective maximum values per campaign (min–max scaling to [0–1]). We assessed the potential influence of WWTP effluent discharge, combined sewer overflows (CSOs) and rainfall by descriptive analysis and comparing discharge volumes to results from MP load.

3 Results and discussion

3.1 Sampling conditions

Figure 3 A-E presents the river discharge time series over the complete monitoring period and details the flow conditions of each sampling site by sampling campaign. Extreme precipitation in July 2021 in western Europe led to increased river discharge during the sampling campaign Jul-2021 (median at Paris Austerlitz: 446 $m^3\ s^{-1}$), which was supposed to be a low summer flow. In fact, Jul-2021 showed highest median river discharge of all campaigns. The maximum recorded precipitation in Paris center during a Jul-2021 sampling was 43.3 mm d^{-1} (July 13) and rain fell in the first two days of this campaign, it was dry otherwise. Nov-2021 flow conditions were still relatively low (median at Paris Austerlitz 247 $m^3\ s^{-1}$) due to a month-long dry period in fall 2021. Precipitation was recorded at the beginning of the Nov-2021 campaign with a maximum of 13.7 mm d^{-1}. River discharge was higher in Feb-2022 with 378 $m^3\ s^{-1}$ (median at Paris Austerlitz), but lower than the winter discharge multi-annual mean in February of about 580 $m^3\ s^{-1}$ (Flipo et al., 2020) and far below the high-flow 5-year daily average rate (1,400 $m^3\ s^{-1}$) even though it was rainy throughout this sampling campaign (average: 1.6 mm d^{-1}). Jul-2022 flow conditions were low (median at Paris Austerlitz 91 $m^3\ s^{-1}$) and representative for summer conditions. Rainfall was only recorded on the first and third day of sampling with a maximum of 17.2 mm d^{-1} upstream. The overall flow conditions contrasted with the usual river flow seasons of the Seine. Therefore, Jul-2021 and Feb-2022 are further considered high flow (HF) campaigns, Nov-2021 medium flow (MF) and Jul-2022 low flow (LF) campaigns. The largest differences of river discharge between sampling sites were in the high flow campaigns Jul-2021 (range: 52–719 $m^3\ s^{-1}$) and Feb-2022 (range: 70–628 $m^3\ s^{-1}$). Despite the randomized sampling order, river discharge increased from upstream to

downstream during each campaign, reflecting the river's natural progression. Physical water parameters reflected the conditions expected during the seasons with higher water temperatures in summer than in winter (Supplementary Information (SI) Table SI 1Figure SI 1). Feb-2022 exhibited highest pH-values and they decreased downstream in all campaigns and were negatively correlated with water temperature. Conductivity levels increased along with the sampling sites and were similar throughout, slightly higher in Jul-2022. At CSO location Clichy and La Briche ~12 Mm^3 and 883 Mm^3 of effluent from WWTPs were discharged into the Seine during the 13-months monitoring period (July 2021 – July 2022). In alignment with precipitation larger volumes of CSO were released in July 2021 and WWTP effluents were enhanced.



Campaign	Min – max (median) river discharge ($m^3 s^{-1}$), data measured at the hydro station close to each sampling site	Median river discharge ($m^3 s^{-1}$) at Paris Austerlitz
Jul-2021	52 – 719 (405)	446
Nov-2021	48 – 327 (213)	247
Feb-2022	70 – 628 (358)	388
Jul-2022	23 – 138 (92)	91

Figure 3 (A) River discharge (Q) over the course of 14 months for different hydrological stations; sampling dates are indicated per relevant station (circles); river discharge (Q) is displayed for campaign 07/2021 (B), 11/2021 (C), 02/2022 (D) and 07/2022 (E), from two weeks period prior to the first sampling per campaign until the last sampling. The relevant river

discharge for both sampling sites S3 and S4, is 'La Seine à Austerlitz'. Median values of river discharge per campaign in the attached table.

3.2 Microplastics before, mid, and after Paris

3.2.1 Spatiotemporal variation of MP concentrations

The number concentrations of MPs in all samples ranged from 14 to 4,668 particles m^{-3} (see Table 2 and Figure 4) and the mass concentrations ranged from one to 962 µg m^{-3}. Sixteen types of polymers, ranging from low-density PE to high-density PVC, were detected across the entire size range of the analysis [25-300µm] (see sections 3.2.2 and 0). For sampling sites in the Seine River, the median MP number concentrations were highest in Jul-2021 (958 particles m^{-3}) followed by Nov-2021 (847 particles m^{-3}), Feb-2022 (678 particles m^{-3}), and Jul-2022 (283 particles m^{-3}). Mass concentrations were also highest in Jul-2021, followed by Nov-2021, Feb-2022, and Jul-2022. At the Marne River site (M1), MP number and mass concentrations ranged from 16 to 1,651 particles m^{-3} and one – 307 µg m^{-3}, respectively, and were highest in Nov-2021, followed by Feb-2022, Jul-2022, and Jul-2021.

The highest MP concentrations in the Seine were detected in the HF campaigns Jul-2021 and Feb-2022 and the lowest in the LF campaign Jul-2022, suggesting hydrological influences (see Figure 5 A). Within campaign, MP number and mass concentrations differ by one to two orders of magnitude, indicating high variability. The concentrations of MP increased from the upstream to the urban area and remained high downstream (see Figure 5 B), indicating that Greater Paris contributes to MP pollution in the Seine. The median concentration at the upstream site (S1) was significantly lower ($p<0.01$) than at urban sites (S2-S5), at 58 particles m^{-3} compared to 726 particles m^{-3}. The highest median MP concentrations were measured at urban sites S3 and S4 (1,208 and 1,164 particles m^{-3} respectively). The lowest MP concentrations were measured at S1 in all sampling campaigns. Higher MP levels were occasionally observed downstream (S6). This urban pattern varied between campaigns. In the HF campaigns (Jul-2021 and Feb-2022) MP concentration peaked at urban sites and downstream, remaining high. In the MF and LF campaigns (Nov-2021 and Jul-2022), peaks were observed at urbans sites, but concentrations decreased downstream (S6). The observed spatial patterns were not linear and fluctuations in MP concentrations were observed.

Previous studies in the Seine River reported median MP concentrations between 30 [80-5,000 µm] and 15,500 particles m^{-3} [80-500 µm] (Treilles et al., 2022) (Dris et al., 2015b), which are in the same order of magnitude, but up to 16-times higher as results in this study. The MP concentrations in the Seine were also comparable to measurement in other large European rivers, spanning several orders of magnitude from 0.15 particles m^{-3} [70-5,000 µm] in the Garonne River to 29,000 particles m^{-3} [25-5,000 µm] in the Loire (Vidal et al., 2023). MP concentration ranged from 16 to 1,707 particles m^{-3} [25-300 µm] in the canals of Amsterdam (Sefiloglu et al., 2024) where there same sampling and analytical methods were used. Similar median MP abundances as observed in this study were reported for the Dommel and Meuse rivers (654 and 867 particles m^{-3} respectively [20-300 µm]) (Mintenig et al., 2020). In rivers Elbe, Rhine and Thames, MP concentrations ranged between 4 and12,000 particles m^{-3} for particles between 50 and 5,000 µm] (de Carvalho et al., 2021; Devereux et al., 2023; Erni-Cassola et al., 2024; Scherer, Weber, et al., 2020).

Multiple studies found a strong presence of MPs in urban rivers but without a clear spatial or temporal trends (Dris et al., 2015b; Rodrigues et al., 2018; Treilles et al., 2022; Valine et al.,

2020) (Elert et al., 2017; Mintenig et al., 2020) A study in Taiwanese rivers established linked increased MP abundance along the urban gradient to higher population density and storm sewers as MP-emitting sources (Kunz et al., 2023). Some studies have reported seasonal patterns and explanations included hydrological impacts, temporal MP emissions, or seasonal differences in outdoor activity (Li et al., 2023; Mani & Burkhardt-Holm, 2020; Moses et al., 2023; Sefiloglu et al., 2024; Treilles et al., 2022). The multitude of influences on MP release, fate, and transport could explain MP trends or variations, especially in urban areas (Birch et al., 2020). In addition, considerable inconsistencies in methodologies, target MPs, and reporting hamper comparability across studies.

Table 2 MP concentration (particles m^{-3}) in the Seine and Marne River across sampling sites and campaigns with mass concentration (in µg m^{-3}) per sample (in parentheses). Below median values of MP (mass)concentration in the Seine River (S1-S6) by campaign (N=6). Variation for MP concentration by site and campaign was calculated as (Max -Min)/Min *100.

	Sampling campaign				
Site	**Jul-2021**	**Nov-2021**	**Feb-2022**	**Jul-2022**	**Median**
S1	19 (4)	128 (46)	97 (31)	14 (2)	58 (18)
S2	145 (32)	903 (148)	798 (239)	623 (80)	711 (114)
M1	16 (1)	1,651 (307)	799 (197)	188 (61)	494 (129)
S3	4,668 (962)	1,859 (394)	557 (132)	142 (20)	1,208 (263)
S4	643 (133)	1,668 (407)	1,672 (421)	659 (151)	1,164 (279)
S5	2,599 (405)	792 (142)	403 (50)	425 (79)	609 (111)
S6	1,273 (285)	348 (57)	4,392 (822)	134 (13)	811 (171)
Median MP (mass) concentration	958 (209)	847 (145)	678 (186)	283 (49)	
Min - max MP concentration	19 – 4,668	128 – 1,859	97 – 4,392	14 – 659	
Min - max MP mass concentration	4 – 962	46 – 407	31 – 822	2 – 151	

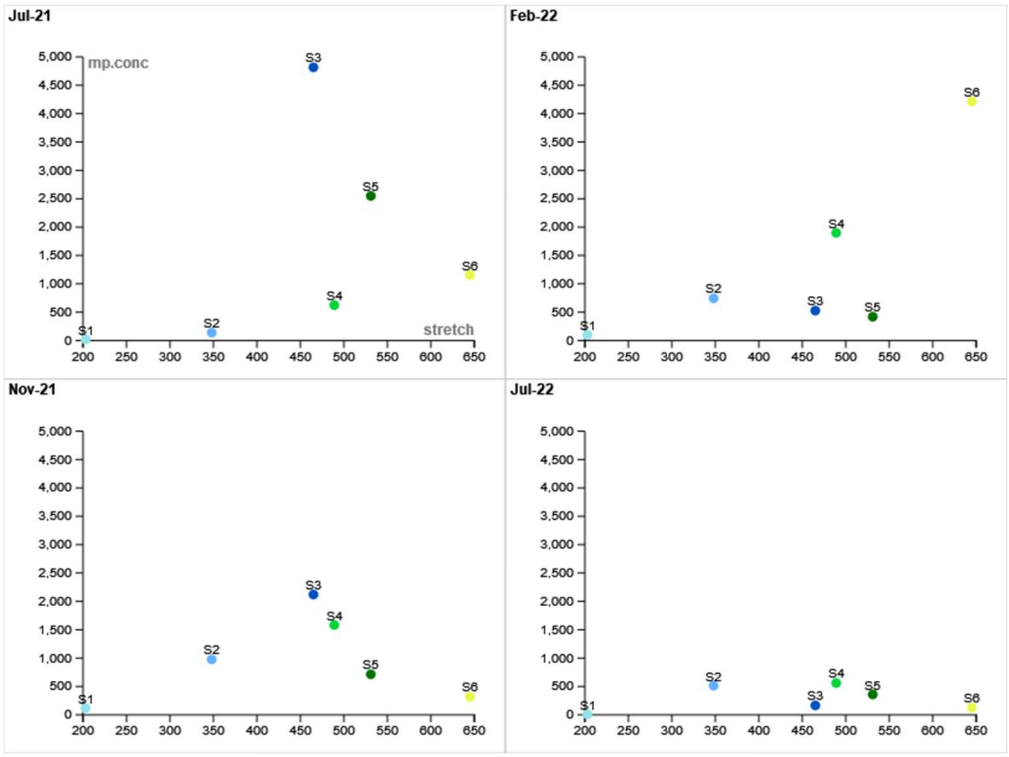


Figure 4 MP concentrations (y-axis, in particles m^{-3}) per sample (color and label) along the Seine River stretch (bottom x-axis, in km) displayed for each sampling campaign (Jul-2021, Nov-2021, Feb-2022, Jul-2022).

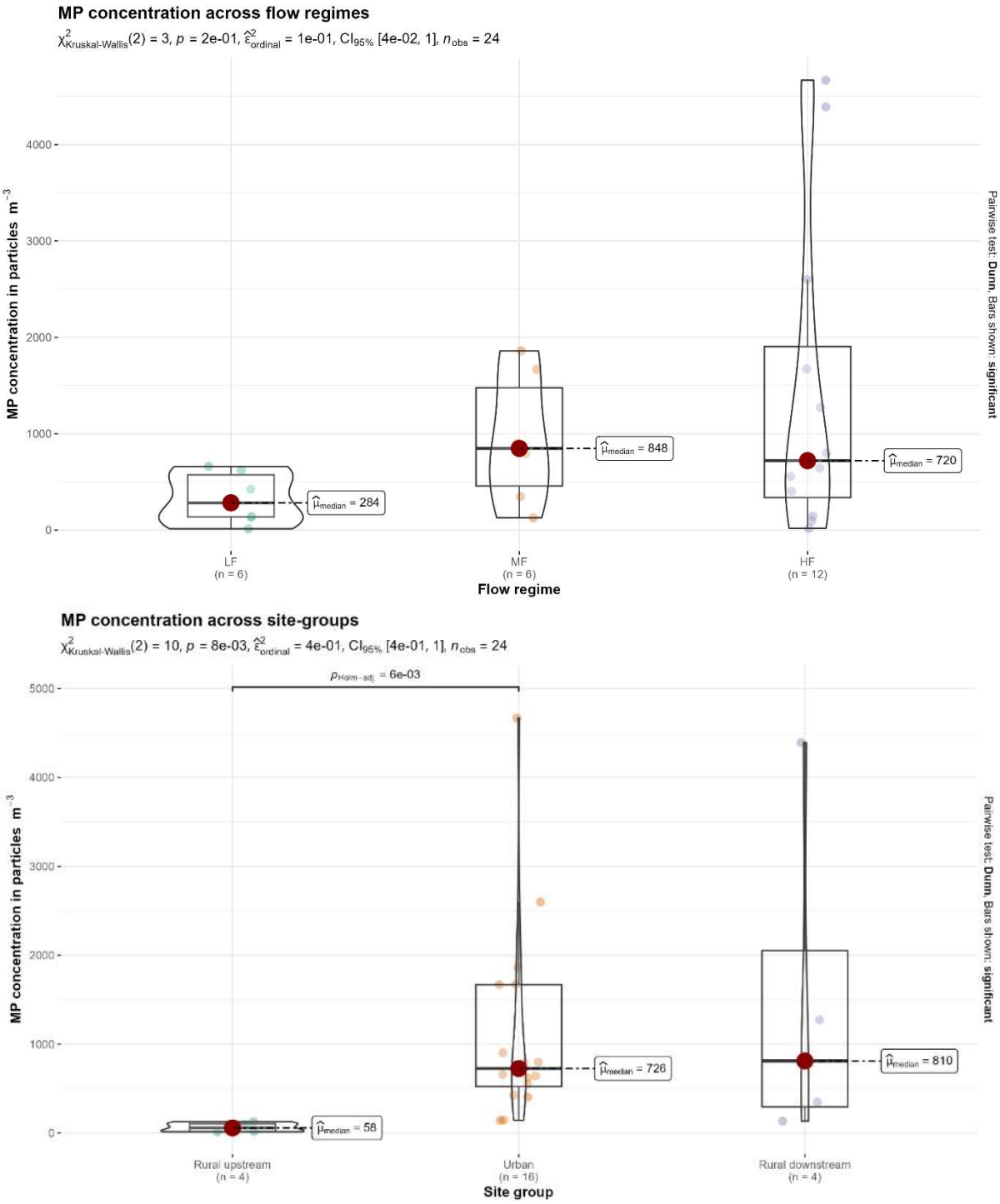


Figure 5 Differences in MP concentrations across flow regimes low flow (LF), mid flow (MF), high-flow (HF) (A) and across site groups Rural upstream (S1), Urban (S2-S5), Rural downstream (S6).

3.2.2 Polymer types

Sixteen polymer types were identified in all samples with PP, PE, and PS covering ~90% (Figure 6). Concentrations of PP, PE and PS ranged from 0 – 3,066 particles m^{-3}. The MP concentrations of all 'other' polymer types span 0 – 136 particles m^{-3}. PVC and polyester were

most abundant among ‘other’ polymer types (~50% in this group). MP number and mass concentrations of each polymer type and the detection frequency (i.e., the number of detected polymer types) in all samples are presented in Table 3 and Table 4, respectively. Spatial trends observed previously are also valid for the MP concentrations of the three main polymers. ‘Other’ polymer types occur more often and in higher concentrations at urban and downstream sites and rarely at S1. The early urban site S2 had few ‘other’ polymers. For example, S3 and S4 exhibit high MP concentrations of PP, PE, PS, PVC and PU, as well as relatively high concentrations of acrylic, and polyester. Acrylic paints, cellulose acetate, epoxy and vinyl copolymer occurred only occasionally and in low concentrations (1-14 particles m^{-3}) at sites S3 and S4. The detection frequency at sites increased toward downstream in Jul-2022, Feb-2022 and Jul-2022, but not Nov-2021. A high number of different polymer types (ranging from 8-13) was observed at all sites in Nov-2021. When Nov-2021 was excluded from analysis, detection frequency at S1 was significantly lower compared to S4 and S6 (p-value = 0.03, N=18,Table SI 2). Table SI 4 summarizes the median number and mass concentrations and the proportions of the different polymer types per campaign.

PP, PE, and PS are most used polymers worldwide (Plastics Europe, 2025). Those three polymers are dominating MP pollution in river systems like the Rhine or Garonne, and studies reported similar proportions as observed in this study (Erni-Cassola et al., 2024) (Mintenig et al., 2020) de Carvalho et al. (2021). Treilles et al. (2022) reported up to 14 polymer types in the Seine with PP>PE as the two most abundant polymer types [80-5,000µm], and PET (i.e., polyester) as third most common type. Similar detection frequencies were reported in two Dutch rivers (Mintenig et al., 2020). Also, PVC, polyester and acrylic are frequently reported in rivers (Koelmans et al., 2019). The consistent occurrence of PP, PE and PS, ABS, acrylics, or PVC at urban and downstream sites suggest ongoing inputs into the river. Polymer types can be related to urban sources, such as ABS and SBR to traffic, or acrylics, PVC, PVAC epoxy to construction and paints, or PU and PA being often related to textiles.

Table 3 MP concentrations (in particles m^{-3}) per Seine sample for each polymer type. The sum is calculated per sample, and the detection frequency (Freq.) is given, as the count of the different polymer types that were detected in a sample (number of polymer types).

Sampling campaign	Site	ABS	Acrylic	Acrylic paints	Alkyd	Cellulose acetate	Epoxy	PA	PE	Polyester	PP	PS	PU	PVAC	PVC	SBR	Vinyl copolymer	Sum	Freq.
Jul-2021	S1	0	0	0	0	0	0	0	3	0	16	0	0	0	0	0	0	19	2
	S2	0	0	0	0	0	0	0	10	0	124	10	0	0	0	0	0	144	3
	S3	0	41	0	0	0	14	0	909	27	3,066	448	0	0	136	27	0	4,668	8
	S4	0	0	0	0	0	0	0	41	8	561	16	8	0	8	0	0	642	6
	S5	10	10	0	0	0	0	10	663	0	1,427	418	0	0	31	31	0	2,600	8
	S6	22	4	0	4	0	0	4	330	0	604	260	18	0	22	4	0	1,272	10
Nov-2021	S1	1	0	0	0	0	0	0	61	1	48	12	1	0	1	1	1	127	9
	S2	0	11	0	6	0	0	3	161	25	642	36	6	0	14	0	0	904	9
	S3	3	18	3	3	0	0	3	423	18	1,141	210	11	3	21	0	3	1,860	13
	S4	0	34	0	17	0	0	0	168	34	1,062	270	51	0	34	0	0	1,670	8
	S5	9	7	0	2	0	0	4	109	2	499	160	0	0	0	0	0	792	8
	S6	3	3	0	0	0	0	0	39	3	226	62	7	0	3	0	0	346	8
Feb-2022	S1	0	0	0	0	0	0	0	44	0	53	0	0	0	0	0	0	97	2
	S2	0	0	0	0	0	0	0	209	5	514	64	0	0	5	0	0	797	5
	S3	0	0	0	0	0	0	0	122	8	367	38	13	0	8	0	0	556	6
	S4	8	11	0	0	0	0	5	473	11	972	122	40	3	26	3	0	1,674	11
	S5	0	0	0	0	0	0	0	58	23	276	46	0	0	0	0	0	403	4
	S6	23	34	0	0	0	0	0	1,227	57	2,615	390	11	0	23	11	0	4,391	9
Jul-2022	S1	0	0	0	0	0	0	0	3	0	12	0	0	0	0	0	0	15	2
	S2	2	0	0	0	0	0	0	73	0	434	109	0	5	0	0	0	623	5
	S3	0	0	0	0	0	0	0	12	0	123	7	0	0	0	0	0	142	3
	S4	1	18	0	0	1	0	4	126	13	416	55	8	4	14	0	0	660	11
	S5	0	0	0	0	0	0	0	52	0	288	73	2	0	9	0	0	424	5
	S6	0	1	0	1	0	0	0	11	2	101	17	1	0	0	0	0	134	7

Table 4 MP mass concentrations (in ng L^{-1}) per Seine sample for each polymer type. The sum is calculated per sample, and the detection frequency (Freq.) is given, as the count of the different polymer types that were detected in a sample (number of polymer types).

Sampling campaign	Site	ABS	Acrylic	Acrylic paints	Alkyd	Cellulose Acetate	Epoxy	PA	PE	Polyester	PP	PS	PU	PVAC	PVC	SBR	Vinyl copolymer	Sum	Freq
Jul-2021	S1	0	0	0	0	0	0	0	16	0	4,083	0	0	0	0	0	0	4,099	2
	S2	0	0	0	0	0	0	0	1,751	0	29,553	564	0	0	0	0	0	31,868	3
	S3	0	6,954	0	0	0	4,692	0	451,499	5,525	426,233	53,569	0	0	9,224	4,559	0	962,255	8
	S4	0	0	0	0	0	0	0	33,612	2,982	94,208	444	885	0	1,043	0	0	133,174	6
	S5	173	2,956	0	0	0	0	3,232	156,959	0	173,381	50,467	0	0	2,350	15,830	0	405,348	8
	S6	3,841	1,351	0	1,741	0	0	309	150,512	0	75,878	44,699	1,619	0	3,448	1,492	0	284,890	10
Nov-2021	S1	108	0	0	0	0	0	0	30,784	230	7,367	4,011	205	0	1,601	990	237	45,533	9
	S2	0	2,377	0	622	0	0	217	66,903	5,361	56,627	7,585	5,010	0	3,321	0	0	148,023	9
	S3	67	2,361	1,853	1,531	0	0	265	187,283	2,483	153,374	35,466	917	844	7,379	0	152	393,975	13
	S4	0	6,514	0	1,869	0	0	0	116,283	37,075	161,621	75,906	3,395	0	4,140	0	0	406,803	8
	S5	2,114	775	0	609	0	0	1,179	47,746	1,154	61,159	27,777	0	0	0	0	0	142,513	8
	S6	241	1,152	0	0	0	0	0	18,270	100	30,753	5,686	492	0	131	0	0	56,825	8
Feb-2022	S1	0	0	0	0	0	0	0	26,856	0	4,074	0	0	0	0	0	0	30,930	2
	S2	0	0	0	0	0	0	0	141,003	891	75,136	22,039	0	0	214	0	0	239,283	5
	S3	0	0	0	0	0	0	0	75,556	874	42,700	7,591	1,881	0	3,692	0	0	132,294	6
	S4	3,907	2,438	0	0	0	0	1,511	245,617	1,009	114,903	35,532	6,858	302	6,991	1,877	0	420,945	11
	S5	0	0	0	0	0	0	0	16,090	2,852	23,120	8,026	0	0	0	0	0	50,088	4
	S6	1,569	7,084	0	0	0	0	0	449,490	10,474	264,575	84,737	341	0	1,783	2,123	0	822,176	9
Jul-2022	S1	0	0	0	0	0	0	0	676	0	1,785	0	0	0	0	0	0	2,461	2
	S2	496	0	0	0	0	0	0	23,372	0	34,188	19,377	0	2,626	0	0	0	80,059	5
	S3	0	0	0	0	0	0	0	1,854	0	17,240	547	0	0	0	0	0	19,641	3
	S4	577	3,521	0	0	135	0	1,387	50,369	2,418	63,284	20,355	420	334	8,525	0	0	151,325	11
	S5	0	0	0	0	0	0	0	14,445	0	38,096	21,690	253	0	4,671	0	0	79,155	5
	S6	0	66	0	244	0	0	0	1,854	240	8,702	1,406	17	0	0	0	0	12,529	7

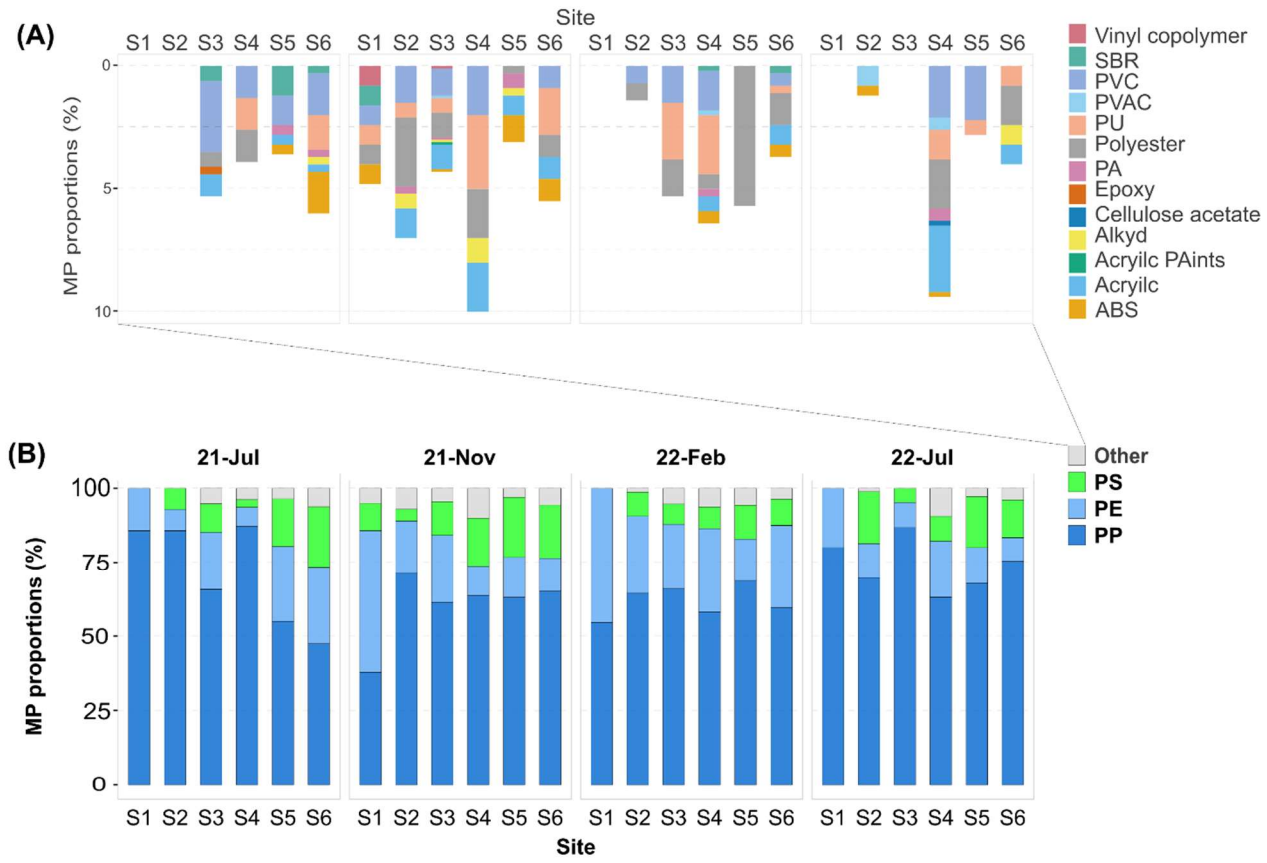


Figure 6 (A) detailed composition of 'Other' polymer types per sample across the four sampling campaigns. (B) Polymer type composition of the three most common polymer types, i.e., PP, PE, PS, and 'Other' polymer types modified after (Stratmann et al., 2024).

3.2.3 MP sizes

The µ-FTIR analysis results showed an overall left-skewed distribution of MP particle sizes (major particle diameter) between 25 and 300 µm (Figure 7 A). This pattern was consistent in all samples regardless of the relative MP concentration (see Figure SI 3). There was a considerable decrease of MPs in the smallest measured size bin [25-50 µm]. The concentration-weighted median of all Seine samples was 81 µm, indicating that smaller particles were more prevalent. Analysis of MP size revealed variations in relation to river flow regimes and morphologies, as shown in Table 5. In terms of time, the median size of MPs was slightly larger in MF conditions (Nov-2021), but the median weight was lower in the LF campaign (Jul-2022). Larger, heavier particles were observed in rural areas upstream (S1). Additionally, MPs were not present in all size ranges at upstream site S1. Median particle sizes varied by polymer type (see Figure SI 4). However, the composition of PP, PE, PS, and 'Other' polymer types across the size bins was comparable in most samples, reflecting an even distribution. The MP size distribution for the Marne River was similar to that of the Seine, as demonstrated in Figure SI 5. This further indicates that MP pollution in the urban area is consistent.

The left-skewed pattern observed in the distribution of MP particle sizes is a common finding in studies that use spectrometric methods to identify MPs (Mintenig et al., 2020; Murphy-Hagan et al., 2025; Rist et al., 2020; Sefiloglu et al., 2024) This pattern can be described as a power-law function (Kooi & Koelmans, 2019). The drop in the smallest size bin is due to uncertainty and underestimation of particles, resulting from the µ-FTIR analysis technique's limit of detection with a minimum pixel size of 25 µm (Rist et al., 2020). The consistency observed in the size distribution and the distribution of polymer types across the size bins suggests that the 'microplastic soup' in the Seine River is homogeneous. Given that S1 is located upstream, the lower input of microplastics (MP) of diverse sizes and fewer polymer types compared to the other sampling sites may reflect the lower impact upstream of Paris.

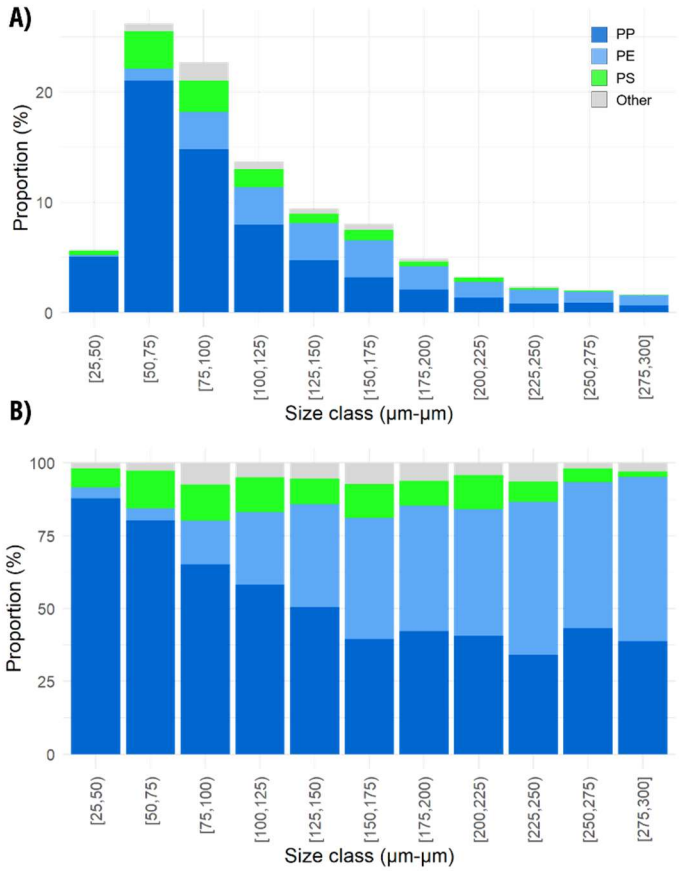


Figure 7 (A) MP size distribution [25 – 300 µm] of all Seine samples in 25 µm-size bins. Bars further show the proportion of the polymers polypropylene (PP), polyethylene (PE), polystyrene (PS) and 'Other', i.e., all other polymer types cumulated. Data is based on the major particle diameter and proportions were weighted by MP concentration. (B) Relative proportions of polymer types (polymer composition) within each size bin. Most prominent was PP, followed by PS, PE and 'Other' made only a few % of the overall composition. Data is based on the major particle diameter and proportions were weighted by MP concentration per sample.

Table 5 Summary statistics of particle characteristics for all Seine sites (S1-S6). Particle major diameter (Major) and particle mass (Pmass). LF = low flow, MF = mid flow, HF = high flow.

	Major [µm]	Pmass [ng]
Flow regime		
LF (Jul-2022)	81	65
MF (Nov-2021)	96	83
HF (Jul-2021, Feb-2022)	81	80
Morphology		
Rural upstream (S1)	115	116
Urban (S2-S5)	81	78
Rural downstream (S6)	81	73

3.3 Hydrology

3.3.1 River discharge and MP concentration

A positive correlation ($\rho = 0.7$, $p < 0.01$; Figure SI 1) was found for MP concentration and Seine River discharge (N=24) overall consolidating the observed differences between high (HF), mid (MF), and low flow (LF) sampling campaigns. This finding is a valuable insight into MP dynamics and corroborates observations with high river discharge and MP concentrations in July 2021 and February 2022. These results suggest that for Jul-2021, a campaign with a strong influence from extreme precipitation, the introduction and mobilization of MP by high flow conditions was likely. A more robust assessment of each sampling site for river discharge and MP concentration across campaigns it not possible due to the small sample size (N=4). Visualizations suggest positive trends of MP concentration and river discharge at sites S1, S3, S5 and S6 (Figure SI 7). These results support the generic hypothesis that river discharge impacts MP concentrations, but there was not enough data to gather stronger evidence.

An overall correlation of year average discharge and MP concentration [sizes 0.3–5 mm] in the Rhine River has been observed as well as a general downstream increase in mean MP abundance (Mani & Burkhardt-Holm, 2020). The positive trend at two of the sampling sites indicated the importance of hydrologically driven MP input or mobilization mechanisms at those sites. Higher plastic debris in the Seine was reported after increased rainfall with higher MP concentrations on the water surface (Dris et al., 2015b). However, the overall few/weak correlations at individual sites suggests that other factors may be more influential than discharge alone. In the Rhine River, no correlation was found for river discharge and MP concentration (Erni-Cassola et al., 2024). They argue that local or other chemo-dynamic factors like MP resuspension may play a bigger role.

Another study observed that river discharge did not affect MP concentrations, but only MP fluxes, in the Seine River (Treilles et al., 2022). In this study, river flow conditions were not very high (max. 719 $m^3 s^{-1}$) with 50% of the samplings below 231 $m^3 s^{-1}$ (Figure SI 6). There were only five samplings (21%) with Seine discharge above 400 $m^3 s^{-1}$. The few measurements for higher river discharge limited the correlation assessment. Larger sample size across a larger spread of river discharge values would improve such analysis. We conclude that river discharge is no silver bullet to predict MP concentrations in the Seine River, but that additional data is needed to further assess the relationship between river discharge and MP concentrations.

3.3.2 Insights into microplastics through suspended solids

To understand whether MP particles could be linked to the observation of solid particles in the water column we assess suspended solids concentration (SSC) and turbidity with MP mass concentration. Turbidity and SSC correlated strongly (ρ=0.81), and both showed a positive correlation to river discharge throughout. Interestingly, the river discharge conditions were best reflected in turbidity (ρ=0.73). For all Seine sampling points cumulated, SSC correlated moderately with river discharge ($\rho = 0.64$, Figure SI 1) but not with MP mass concentration. No trend of SSC or turbidity was obvious along the sampling site gradient. SSC medians alternate across campaigns in line with river discharge median values. When analyzed by sites, a visual trend of increasing MP mass concentrations with SSC was found at site S6, but not at other sites and not in the various campaigns. Turbidity, however, showed a positive correlation with MP concentration at high-flow sampling campaign Jul-2021 ($\rho = 0.94$, $p<0.01$) but not at other campaigns. The highest turbidity was detected at S3 and S5, sites which both held highest MP concentrations during this campaign.

SSC and turbidity measure distinct aspects of suspended matter: SSC quantifies suspended particle mass (gravimetric), while turbidity reflects optical properties (light scattering). The stronger correlation with turbidity than with SSC indicates that MPs may be more associated with optically detectable particles than with the mass of suspended solids. The overall weak alignment with MPs under LF and MF conditions indicates that MPs do not simply follow solid dynamics in the upper water layer but are instead mobilized primarily during extreme hydrological events. Sullivan et al. (2023) found positive correlations of MP concentration with suspended particulate matter and turbidity in a river estuary. A similar observation has been made by Mohsen, Balla, and Kiss (2023) finding the relationship of SSC and MP enhanced in flood events when discharge was high. They argue that this may reflect that processes influencing MP concentration, like runoff and riverbed turbulences, contribute more during intense discharge conditions (including floods) than in lower flow conditions. In the latter case, other processes like wastewater inflow may be more relevant. The resuspension of sediment-bound MPs, for example, is likely to occur during higher discharge conditions, due to increased turbulence and shear-bed stress ((Waldschläger, 2020; Yang & Foroutan, 2023). Such processes could also occur more locally depending on the riverbank, riverbed infrastructure (bathymetry), the amount of sediment, discharge inflows, or shipping activities (Vilmin et al., 2015). SSC or turbidity is not inferior to river discharge and, as explained earlier, other processes can lead to heightened SSC or turbidity (Meybeck et al., 1999).

3.4 MP fluxes and urban release pathways

3.4.1 Spatiotemporal variation of MP loads

The MP fluxes ranged from 300 to 2.7 x 10^6 particles s^{-1} and MP mass fluxes from 46 to 516 x 10^3 µg s^{-1} (Table 6). MP fluxes were highest in the HF (228×10^3 particles s^{-1}), followed by MF (183×10^3 particles s^{-1}) and LF (28×10^3 particles s^{-1}) regimes (Table 7). The same trend was found for MP concentrations (see 3.2.1). In the LF campaign MP loads were significantly lower than in HF samples ($p<0.05$, Figure 8). Maximum MP (mass) fluxes were reached in Feb-2022 (2,758×10^3 particles s^{-1} and 516×10^3 µg s^{-1}), equaling fluxes up to 15.8 t y^{-1}.

Over the total monitoring period, the MP loads increased from upstream to urban and reached highest downstream values (median: 522×10^3 particles s^{-1}), indicating pollution increased along the river (Table 8, Figure 9). Lowest MP fluxes were consistently found upstream (S1) with a median of 3.5×10^3 particles s^{-1}, corresponding to a median mass load of about 1,1×10^3 µg s^{-1}. At urban sites the median MP flux was estimated to 209×10^3 particles s^{-1}, and mass fluxes were 41×10^3 µg s^{-1}.

In Feb-2022, downstream (S6) fluxes were influenced by extremely high MP concentrations (>4,000 particles m^3) in combination with higher river discharge (~630 m^3 s^{-1}). When the data were analyzed without the Feb-2022 campaign, MP (mass) fluxes peaked in the urban area (180×10^3 particles s^{-1}) but decreased downstream to 129 x 10^3 particles s^{-1}, indicating stronger MP pollution in the urban center. The occasionally higher MP load observed downstream (S6) indicates the importance of periodically happening events.

The mass fluxes in this study were three orders of magnitude lower as findings during a flood event in the Seine with river discharge up to 1500 m^3 s^{-1} with about 58 – 1,675 t y^{-1} (min-max) (Treilles et al., 2022). (Treilles et al., 2022) observed a similar upstream to downstream evolution of MP load with higher pollution in urban areas and downstream. Results consolidate the contribution of Greater Paris to MP pollution in the Seine. Studies report annual mass fluxes in rivers around hundreds of tons (Imbulana et al., 2024) (Eo et al., 2019). Multiple studies reported seasonal changes in MP fluxes (Constant et al., 2020; Eo et al., 2019;

Imbulana et al., 2024) often driven by hydrological conditions (e.g. rainfall), sewer inflows, or unexplained. Observations of a flood event in the Seine showed that large MP fluxes were mobilized (Treilles et al., 2022), similar to the observations during the extreme rain in July 2021. During high flow periods, especially smaller MPs are prone to be mobilized and transported downstream (Nizzetto et al., 2016; van Emmerik et al., 2022). The extreme rainfall and high river flow in July would also increase macroplastics mobilization and downstream transport (van Emmerik et al., 2019) adding MPs through fragmentation. MP load was driven by river discharge (Treilles et al., 2022), similar to observation in this study with higher load in HF regimes. The fluctuations in MP load indicate that other MP release, retention, or mobilization processes are of importance. Urban sewer discharges could play a vital role in Paris (see 3.4.3). (Kukkola et al., 2023) showed that temporary river management, like diversion of water for irrigation, has an important impact on the MP load in rivers, as well.

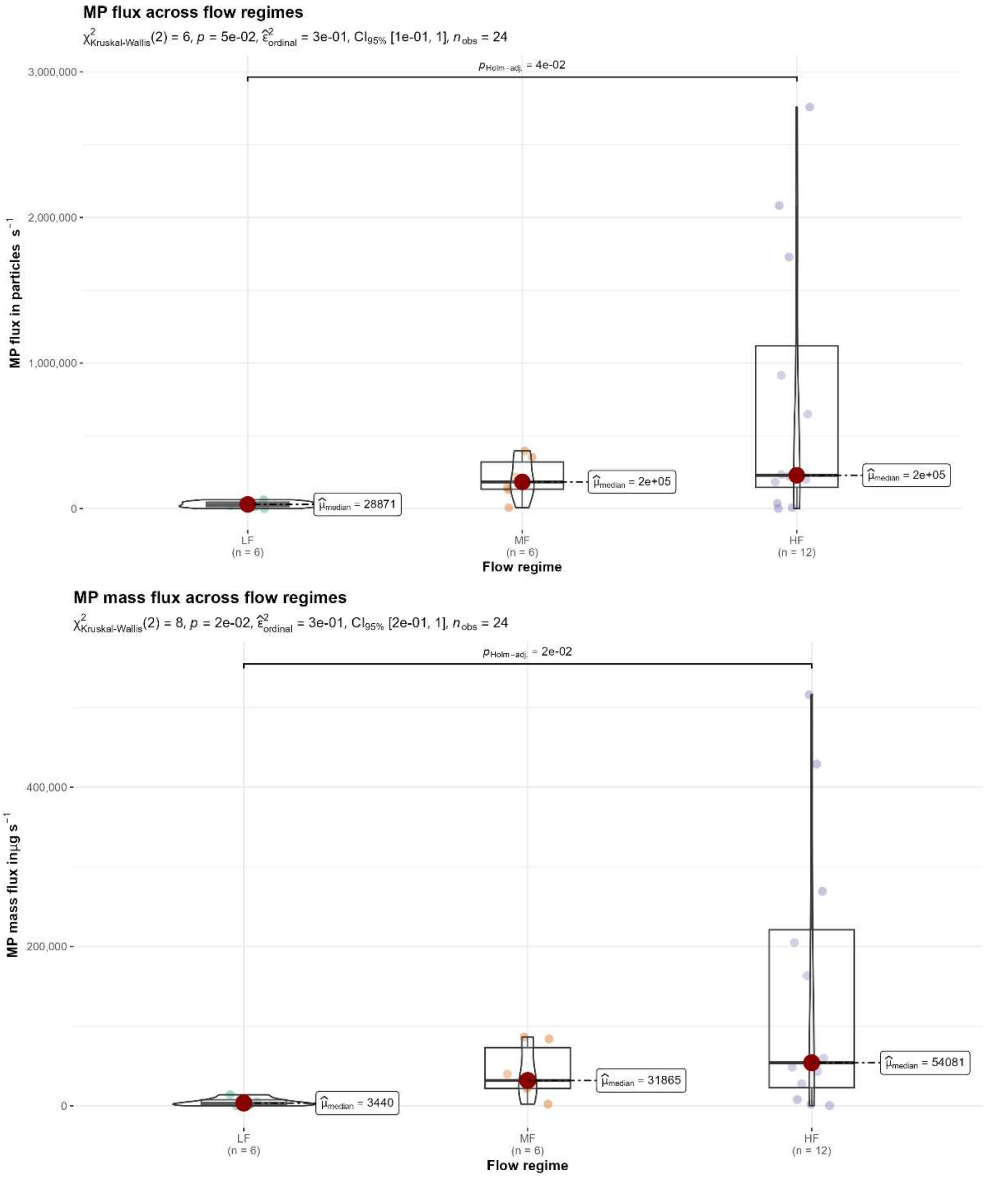


Figure 8 MP fluxes and mass fluxes grouped by flow regime, high (HF), mid (MF), and low flow (LF).

Table 6 MP fluxes (particles s^{-1}) in the Seine River across sampling sites and campaigns with mass flux (in µg s^{-1}) per sample (in parentheses). Below median values of MP (mass)flux in the Seine River (S1-S6) by campaign (N=6). All values in thousands (10^3).

Site	Jul-2021	Nov-2021	Feb-2022	Jul-2022	Median
S1	1 (0.2)	6 (2)	7 (2)	0.3 (0.05)	3.5 (1)
S2	36 (8)	146 (24)	200 (60)	39 (5)	93 (16)
M1	1 (0.06)	122 (23)	88 (22)	4 (1)	46 (12)
S3	2,082 (429)	396 (84)	183 (43)	13 (2)	289 (64)
S4	234 (48)	354 (86)	649 (163)	61 (14)	294 (67)
S5	1,729 (270)	220 (40)	224 (28)	46 (9)	222 (34)
S6	915 (205)	129 (21)	2,758 (516)	18 (2)	522 (113)
S6 (without Feb-2022)	*915 (205)*	*129 (21)*	-	*18 (2)*	*129 (21)*
Median MP (mass) flux	575 (127)	183 (32)	212 (52)	29 (3)	

Table 7 Median MP (mass) fluxes of all Seine samples for different flow regimes. high (HF), mid (MF), and low flow (LF), N=24.

LF			MF			HF		
MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (kg y^{-1})	MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (t y^{-1})	MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (t y^{-1})
28,871	3,440	0.11	183,231	31,865	1.00	228,859	54,081	1.71

Table 8 Median MP mass fluxes (MP load) of all Seine samples for different urban settings. N=24.

	Rural upstream			Urban			Rural downstream		
	MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (t y^{-1})	MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (t y^{-1})	MP fluxes (particles s^{-1})	MP mass fluxes (µg s^{-1})	MP mass fluxes (t y^{-1})
All campaigns included	3,566	1,189	0.04	209,838	41,525	1.31	522,372	113,060	3.57
Feb-2022 excluded	988	208	0.01	183,231	31,865	1.00	129,456	21,204	0.67

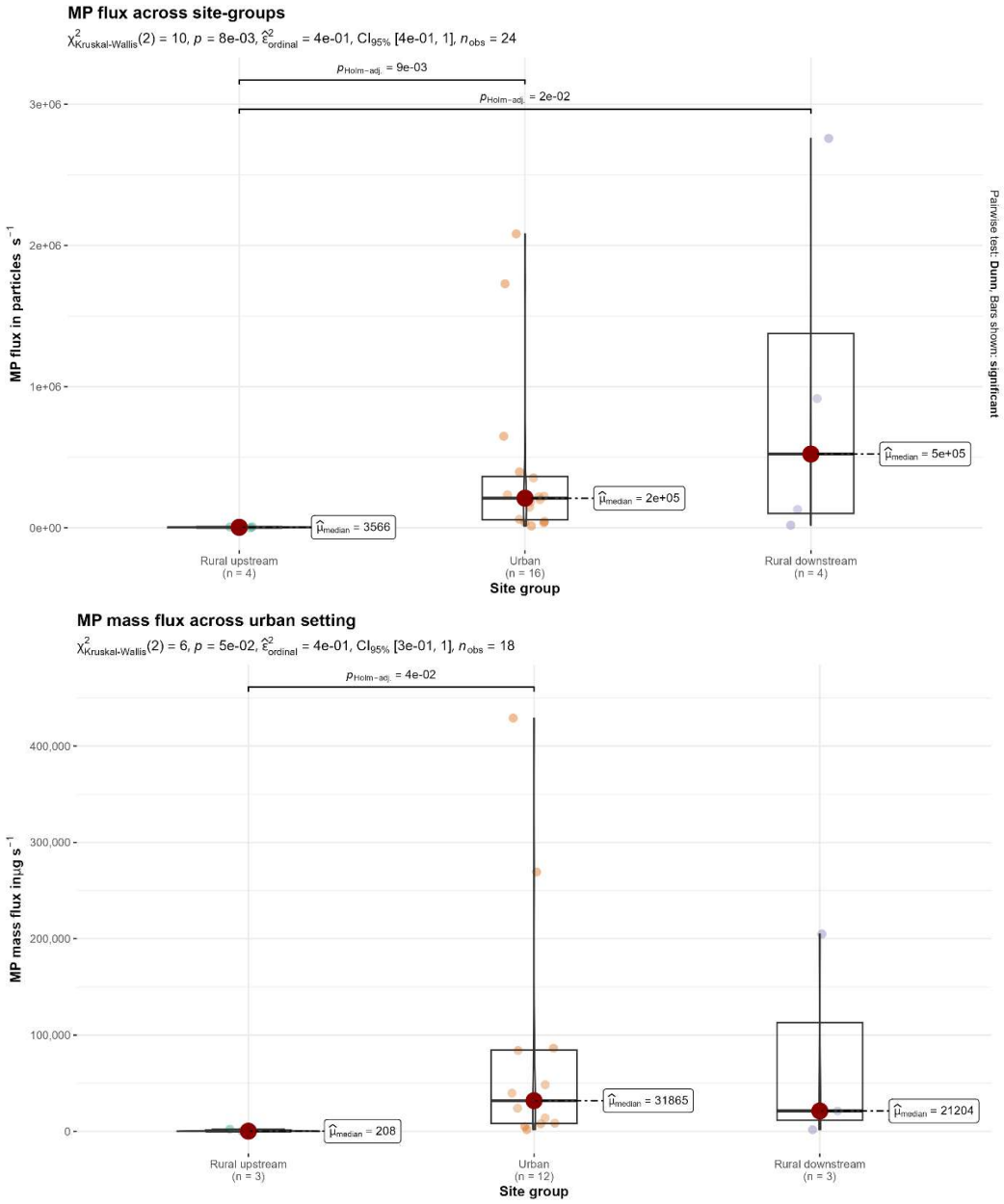


Figure 9 Differences in (A) MP fluxes and (B) MP mass fluxes across site groups (urban setting).

3.4.2 MP mass flux balance

Sankey diagrams display the mass flux evolution of MPs between consecutive sampling sites for each sampling campaign indicating MP 'sinks' or 'sources' indicated as 'MP mobilized' (Figure 10). For better readability, the mass fluxes were converted to kg day^{-1}. Radar plots visualize the interplay between river discharge, MP concentration, and MP flux for each campaign and site to support the interpretation of upstream-downstream MP dynamics (Figure SI 7), Table SI 3).

In all campaigns, the MP load increased upstream site S1 and first site in the urban part (S2), indicating that MPs enter the Seine River in this 145 km river stretch. MP masses further enhance towards the urban center (sites S3 and/or S4) in all campaigns, suggesting additional

MP sources and/or mobilization processes. Fluctuations indicate MP retention or mobilization throughout. MP mass fluxes declined towards S5 and S6 apart from strongly enhanced MP mass flux downstream (S6) in Feb-2022. These results indicate MP retention/sinks after the urban center but periodical MP mobilization downstream.

The Jul-2021 campaign was characterized by increasing MP mass fluxes from 0.02 kg day^{-1} (S1) to 0.7 kg day^{-1} (S2), due to increase of MP concentrations (+760 %) and river discharge (+475 %). The largest mass increase occurred between S2 and S3 (37 kg day^{-1}). River discharge doubled from S2 to S3, and MP concentrations rose to 4,700 particles m^{-3}, further suggesting MP input. The MP mass flux at the Marne River (M1) was negligible (<0.01 kg day^{-1}) towards explaining high MP levels at S3. Notable, sampling dates M1 and S3 were a week apart with intense rain influence in between, making a proper assessment difficult in this case. The MP load decreased from S3 to S4 by about 90% indicating MP retention of about 32 kg day^{-1}. The reduced river flow (364 m^3 s^{-1}, -18% from S3) and decreased MP concentrations explain the observation. The Seine River splits into two sidearms ca. 10 km upstream of S4. S4 is located at a smaller part of the southern side at 'Île de la loge' without direct ship impact. It is likely that the specific location influences the flow dynamics and MP occurrence. The MP mass flux was 24 kg day^{-1} at S5 (addition of +19 kg day^{-1} from S4) caused by high river discharge and MP concentrations (665 m^3 s^{-1} and 2.600 particles m^{-3}, respectively). Mass fluxes dropped towards S6 by ~5.5 kg day^{-1}, suggesting MP retention and/or dilution, as river discharge grew (+8%) but MP concentrations were measured 50% lower compared to the S5.

In November 2021, MP mass fluxes increased from about 0.19 kg day^{-1} upstream (S1) to about 7.2 kg day^{-1} at urban sites and decreased steadily downstream (1.8 kg day^{-1} at S6), indicating a strong urban influence. The initial increase seems driven by higher river discharge and MP concentration. S2 and M1 added MP load explaining S3 but additional MP mobilization of ~3 kg day^{-1} was identified. MP mass fluxes halved from S4 to S5, which is further reduced downstream. suggesting MP retention. In February 2022, a 25-fold initial increase of MP load (S1: 0.19 kg day^{-1}) towards S2 was observed, suggesting MP input of 4.9 kg day^{-1}. From S2 to S3 river discharge rose by 30% and MP concentration declined (-30%), leading to lower MP mass fluxes at S3 and indicating MP retention. Peak MP mass fluxes at S4 (+280%) seem driven by MP concentration (+200% from S3) more than river discharge (+18% from S3). A different dynamic was observed from S4 to S5, with increased river discharge (+45%), and lower MP concentration (-50%), indicating MP dilution or retention effects. The MP load being transported downstream from S5 (2.4 kg day^{-1}) on is minor compared to the previous site. At S6, a 10-fold increase in MP concentration dominated the high MP mass fluxes (44.6 kg day^{-1}), indicating an MP source' adding over 42 kg day^{-1}.

The pattern of the MP load development along sites in July 2022 is similar as in Feb-2022, but MP loads are significantly lower: Fluxes peaked at S4, fluctuations throughout sites were observed, and low MP masses were found downstream. The MP load at S1 was 0.004 kg day^{-1}, 100-fold lower than at S2, suggesting additional MP input of 0.4 kg day^{-1}. Due to the timely distance between sampling M1 (27 July 2022) and S2 and S3 (20 and 21 July 2022), it is difficult to evaluate the Marne River contribution. Maximum MP load was 1.2 kg day^{-1} (S4) and declined downstream to 0.16 kg day^{-1} (S6). This declining mass dynamic through increased river discharge (+30%) but lower MP concentrations (-80%) from the urban center suggests steady MP retention along the river.

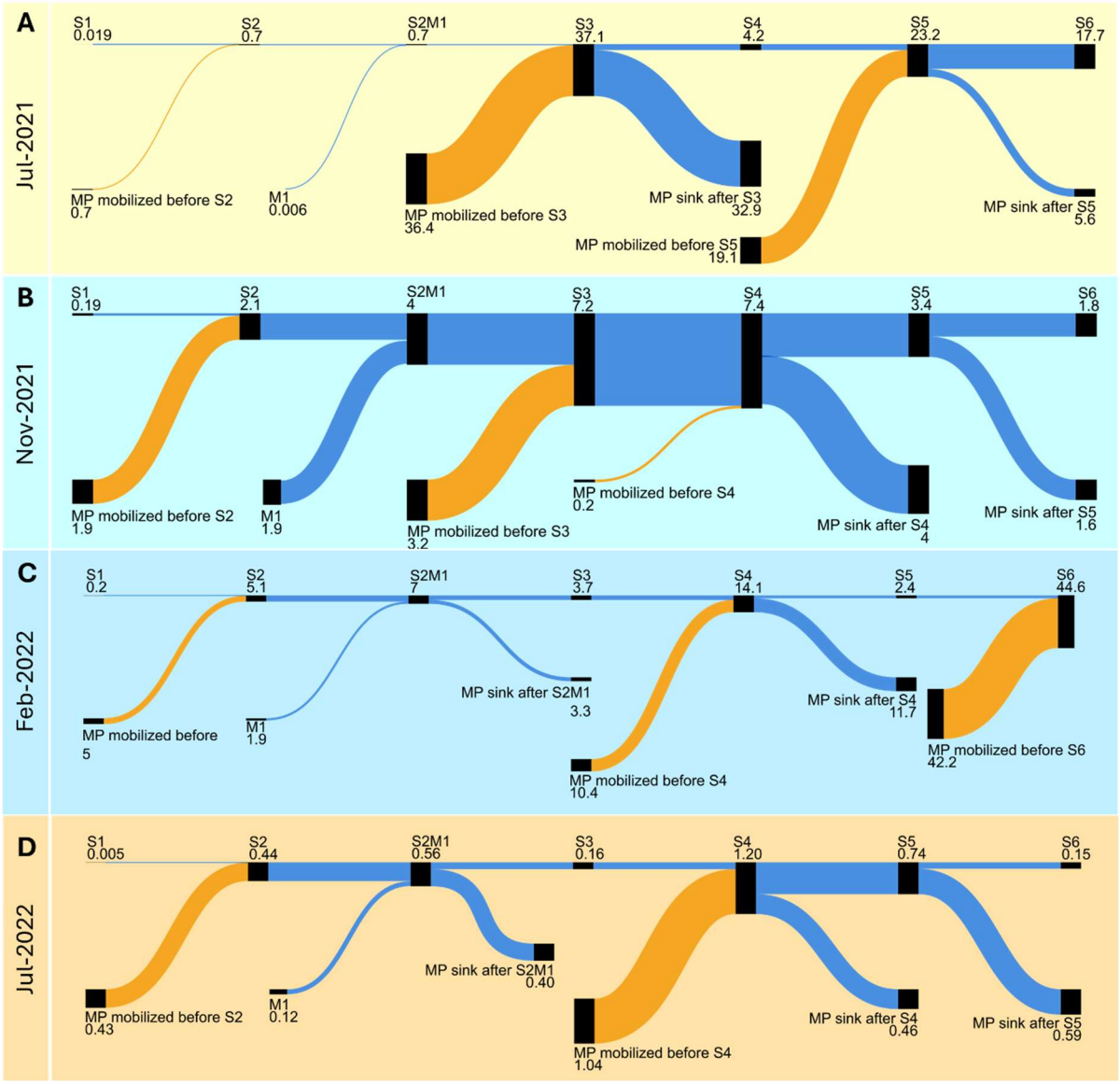


Figure 10 MP mass flux balances across sampling sites for all four sampling campaigns (A-D). Numbers refer to the mass flux of MPs in kg day^{-1}. The unaccounted mass fluxes between consecutive sites are considered either as potential MP mobilized or as MP sink. Dimensions of the line widths not scaled between the graphs.

3.4.3 MP emission tracking

We assessed the potential contribution of urban discharges to the MP load in Greater Paris. Multiple CSOs and enhanced WWTP effluent discharges caused by precipitation were recorded during the sampling periods. Table 9 presents the discharges and precipitation in the relevant period of sampling campaigns. Ten days of CSOs were recorded for La Briche just before or during the samplings with a total of 1.2 Mm^3 but only one two-day CSO event was documented at Clichy in July 2021 with 1.3 Mm^3. The observed CSO volumes during the sampling campaigns reflected 25% (La Briche) and 18% (Clichy) of the discharge at the locations during the 13-month monitoring period. The CSO locations Clichy and La Briche are situated ~20km upstream of S4 (see also Figure 2). WWTP effluents that were released into the Seine in the time of samplings were ~126 Mm^3 (see also Table 5). Sampling site S2 was located 9km downstream WWTP Seine-Amont (SAM) (see also Figure 1). S4 was influenced

by WWTP Seine-Centre (SEC) 12km upstream and S5 was situated 20km after WWTPs Seine-Aval (SAV) and 5km after Seine Grésillons (SEG).

Rainfall from July 10-13, 2021, triggered large CSO discharge at La Briche (1.1 Mm^3) and Clichy (1.3 Mm^3) over a period of several days. Enhanced WWTP effluent discharge was also recorded at SAM, SEC, SAV and MAV over this period. These urban discharges may explain the higher MP load at the urban sites S2, S3 and S5, which were sampled a week after the rainfall. We can assume that the Marne River contributed to the MP load at site S3, given that the WWTP effluent at MAV tripled with the rainfall. As previously mentioned, M1 was sampled just as the rain started on the morning of 12 July 2021. Therefore, the M1 data are not representative of the mass balance at S3, which was sampled on 22 July 2021. The observations indicate that the rain event had an impact on the MP load for several days afterwards, and that MP masses entering through urban discharge are being distributed and/or transported along the Seine River. The increased river discharge during this period may also have triggered various mobilization processes involving MPs, such as sediment resuspension.

The reduced river flow explains part of the decreasing MP load at S4, but local conditions may also be a factor, given that the Seine splits into two sidearms at this point. One possible explanation is that most MPs were transported on the other side, or that a large MP sink could be present. For instance, the calmer conditions at S4 could lead to sedimentation. Alternatively, both processes may be occurring simultaneously. This result shows that MPs can vary, potentially due to local conditions and regardless of urban discharge inflow. In Nov-2021, precipitation was recorded prior to sampling (~2–16 mm), together with combined sewer overflow (CSO) at La Briche (approximately 70 x 10^3 m^3 in four days), and an increase in WWTP effluent volumes at SEC and SAM. The higher MP load observed at urban sites was likely influenced by the urban discharge inflows. There were no other relevant sewer events or strong rainfall during the sampling period. During November, all samples showed an unexpectedly high number of different polymer types. We argue that this observation could possibly have been triggered by the rainfall, but we could not link it directly to urban discharges. There was slight precipitation throughout the entire February 2022 campaign in all areas, with only a few days of heavier rainfall (maximum: 9.3 mm per day). Urban discharges were slightly increased at SAV every other day around mid-February, and one CSO (6,000 m^3) occurred at La Briche on 21 February, which is likely to explain the heightened MP masses at S4. The remarkably high MP concentration at S6 could not be directly attributed to urban discharges. Precipitation was steady and occurred every other day in Paris center and the S6 catchment area. Enhanced WWTP effluent at SAV and CSO at La Briche S6 was observed. This could have introduced MPs, which are now being transported downstream. Alternatively, a temporary MP release or mobilization due to high river discharge conditions could have led to the high MP load at S6. Apart from the rainfall on 19 and 20 July (most pronounced in the S1 catchment at 17 mm per day), the period of the sampling campaign Jul-2022 was dry. Following the rainfall, slightly higher volumes of WWTP effluent were observed at SAV, SAM and MAV, and a CSO event occurred at La Briche (6,000 m^3). The increase in MP load at S2 may be due to discharges from SAM. The larger MP masses at S4 could be explained by enhanced sewer discharges in the urban area.

The increased MP load observed along the Seine River in the four sampling campaigns is caused by MP released via WWTP and CSO discharges triggered by enhanced rainfall. The results align with the higher concentration of MPs in urban areas, where most urban discharges are released into the Seine. (Nguyen et al., 2024) expected that CSOs contribute strongly to MP concentration in the Seine River and estimated MPs from CSOs into the surrounding waters in Paris ranged between 203 – 48 x 10^3 particles m^{-3}. When extrapolating this to data presented

in this study (median MP particle mass = 0,084 µg), the two-day CSO event at Clichy in July 2021 (discharge ~1.3 Mm^3) would have emitted between 22 g and 5.2 kg of MPs into the Seine. With up to 44 kg day^{-1} transported in the urban area of the Seine, this extrapolation lays within a reasonable range. Higher estimations were achieved by (Dris et al., 2018) for CSO site La Briche with about 35 – 3,100 MP fragments L^{-1} which would extrapolate to maximum MP masses of 290 kg during the three-day CSO event (1.1 Mm^3) in July 2021.

MP abundance was also linked with the occurrence of storm sewers in an urban area (Kunz et al., 2023). Several studies investigated the release of MP WWTPs into rivers (Dris et al., 2015a; Dyachenko et al., 2017; Imbulana et al., 2024; Leslie et al., 2017; Schmidt et al., 2020). (Dris et al., 2015b) analyzed treated wastewater from Seine Centre WWTP and found 35,000 MP particles m^{-3} being released, with 60% of the MPs from the washing of clothing in households. WWTP effluent was estimated to account for 20% of annual MP load in the Kamo River catchment. MP load was found to be higher downstream of WWTP effluent location at all sites in a study from (Kay et al., 2018), with similar findings of microfibres being highly present (Dris et al., 2015b). In Amsterdam, WWTP effluents held 51–81 MP particles L^{-1}. Clear results about WWTP emitting MPs were obtained by (Woodward et al., 2021) with findings of untreated sewage from CSOs and treated sewer effluent releasing MPs into UK rivers. They also observed differences in MP assemblages related to certain emitting sources which they describe as a mix of different MP shapes. We observed higher variety of polymer types downstream along the river and enhanced polymer types at all sampling sites in November 2021. No explanation was found but. (Enders et al., 2019) could link certain polymers to the distance to WWTPs but also noted that not all polymers could be assigned to a specific source or release pathway. Particularly, the presence of polymers like SBR (Styrene-Butadiene Rubber), which is identified downstream (S3-S6), could be linked to runoff from urban areas and effluent discharges. Studies like the ones mentioned above could help to explain the occurrence of certain polymer types in the Seine and link them to release pathways or certain spatial features. PE, PP and PS were the most common polymers in the Parisian sewer deposit (median $44x10^3$ particles kg^{-1} DW) (Nguyen et al., 2024). The temporary storage in solid deposits in sewer pipes and accumulation during dry periods causes high release, also seen in high suspended solids concentration, when intense precipitation follows (Tabuchi et al., 2018).

Few studies thus far, including this study, quantify MP fluxes to improve ‘source tracking’ and understanding the mass balance of the MP pollution in relation to various influences throughout the water body and a river catchment (Constant et al., 2020; Dris et al., 2018; Kukkola et al., 2023; Rios-Mendoza et al., 2021; Treilles et al., 2022). The case of a legal release of MP in the Danube River by an industrial plant is a good example for an emitting point source along the river (Lechner & Ramler, 2015). (Kukkola et al., 2023) have found that water diversion, e.g., for drinking water or agricultural use also removes an equivalent number of MPs from riverine surface water and hence, diverts those MPs into other environmental or technical compartments. We argued that MP loads could be explained by the downstream transport of MPs released through urban discharges. However, we currently have no understanding of travel time or route of MP particles in a river system. Closing this research gap would help us to understand the fate of MPs in rivers.

Table 9 Daily WWTP effluent and CSO discharge volumes to the Seine River, and precipitation data (mm) from three stations in the catchment area for the sampling sites, data up to four days prior to and during samplings. WWTPs ordered by location: SAM = Seine-Amont, MAV = Marne Aval, SEC = Seine-Centre, SAV = Seine-Aval, SEG = Seine Grésillons. CSO sites: Clichy, La Briche; Precipitaiton: Melun relevant for S1, Montsouris for S2-S5, Evreux for S6.

Site	Date	SAM	MAV	SEC	SAV	SEG	CLICHY	LA BRICHE	MELUN	MONTSOURIS	EVREUX
	08.07.2021	454,198	63,422	187,479	1,180,000	221,315	0	0	0	0	1.8
	09.07.2021	439,017	62,279	188,611	1,105,000	220,260	0	0	0	0	0
	10.07.2021	424,108	63,422	183,738	1,080,000	218,460	0	0	6.7	0.6	4.4
	11.07.2021	433,329	57,734	181,106	1,090,000	214,140	0	0	0.6	0	0
M1	12.07.2021	653,114	75,291	250,553	1,670,000	278,780	0	24,011	4.6	5.3	6.9
S1	13.07.2021	962,369	119,051	439,612	3,060,000	263,125	945,248	963,406	34.7	43.3	0.4
	14.07.2021	1,004,988	84,800	291,608	2,048,000	261,575	351,306	142,137	0	0.2	0
	15.07.2021	732,453	72,800	135,034	1,328,000	202,510	0	0	0	0	0
S4	16.07.2021	617,137	84,442	172,900	1,260,000	217,490	0	0	0	0	0
	17.07.2021	580,367	79,285	155,724	1,127,000	186,760	0	0	0.2	0	0
	18.07.2021	573,942	76,245	156,090	1,181,000	186,205	0	0	0	0	0
S6	19.07.2021	534,659	71,459	188,200	1,228,000	184,415	0	0	0	0	0
S5	20.07.2021	489,726	65,216	177,746	1,168,000	207,006	0	0	0	0	0
S2	21.07.2021	424,364	58,353	181,589	1,219,000	209,925	0	0	0	0	0
S3	22.07.2021	379,599	56,469	181,589	1,262,000	215,060	0	0	0	0	0
	Sum	**8,703,370**	**1,090,268**	**3,071,579**	**21,006,000**	**3,287,026**	**1,296,554**	**1,129,554**	**46.8**	**49.4**	**13.5**
	29.10.2021	519,605	43,270	344,230	1,497,000	234,785	0	4,936	16.10	7.2	1.80
	30.10.2021	672,085	53,550	330,533	1,686,000	248,700	0	31,246	2.20	5.70	2.80
	31.10.2021	561,357	46,207	305,143	1,461,000	249,070	0	12,753	8.10	4.10	1.40
	01.11.2021	657,551	48,361	359,966	1,623,000	248,700	0	20,144	4	3.8	1.6
M1	02.11.2021	584,050	46,124	268,287	1,225,000	232,160	0	0	13.7	5.6	0
S1	03.11.2021	664,755	41,607	269,485	1,322,000	245,915	0	0	0.4	1.4	1.4
S6	04.11.2021	645,910	44,064	372,375	1,618,000	249,000	0	8,351	3.4	3.6	0.8
	05.11.2021	245,560	38,112	268,778	1,172,000	245,560	0	0	0	0	0
	06.11.2021	483,139	38,573	269,276	1,059,000	244,330	0	0	1.6	0.2	0
	07.11.2021	496,685	42,969	267,685	1,096,000	243,020	0	0	0.2	0	0
	08.11.2021	479,770	39,221	242,175	1,098,000	242,175	0	0	0.2	0.2	0
S2	09.11.2021	470,830	38,522	233,383	1,131,000	241,735	0	0	0.2	0	0
S4	10.11.2021	451,078	35,347	212,897	1,073,000	238,995	0	0	0.6	0.2	0
S5. S3	11.11.2021	471,807	35,496	235,059	1,013,000	243,720	0	0	0.4	0	0
	Sum	**7,404,182**	**591,423**	**3,979,272**	**18,074,000**	**3,407,865**	**0**	**77,430**	**51**	**32**	**10**

	11.02.2022	281,098	61,949	168,423	1,480,000	257,595	0	0	0.2	0	0
	12.02.2022	303,094	59,807	168,104	1,332,000	272,385	0	0	0.2	0	0
	13.02.2022	314,985	61,512	165,093	1,425,000	279,215	0	0	1	0.4	0.8
	14.02.2022	320,499	62,814	165,270	1,780,000	283,335	0	0	9.3	2.4	2.4
M1	15.02.2022	281,182	73,273	167,288	1,536,000	282,830	0	0	0	5.2	3.6
S3	16.02.2022	367,572	76,273	162,930	2,092,000	285,460	0	0	0.4	0.8	1.2
S2	17.02.2022	295,093	65,834	170,238	1,481,000	278,470	0	0	0.4	0.4	0
	18.02.2022	305,411	73,406	169,689	1,848,000	282,755	0	0	0.8	3	1.4
	19.02.2022	300,014	63,402	168,167	1,333,000	278,145	0	0	0	0	0
	20.02.2022	324,172	70,550	164,776	1,698,000	287,335	0	0	4.6	3.4	4.4
S4	21.02.2022	333,973	42,003	168,366	1,491,000	292,800	0	2,186	1	0.2	0
S1	22.02.2022	279,186	37,823	171,519	1,389,000	277,970	0	0	2.2	0.4	1.4
S5	23.02.2022	269,100	37,655	169,681	1,276,000	276,905	0	0	0.8	0.2	0
S6	24.02.2022	316,359	39,712	163,147	1,574,000	281,010	0	0	0.8	2.4	1.8
	Sum	**4,291,738**	**826,013**	**2,342,690**	**21,735,000**	**3,916,210**	**0**	**2,186**	**22**	**19**	**17**
	16.07.2022	353,523	44,323	0	1,106,000	292,105	0	0	0	0	0
	17.07.2022	353,084	44,758	0	1,092,000	291,505	0	0	0	0	0
	18.07.2022	364,312	45,580	0	1,267,000	291,065	0	0	0	0	0
	19.07.2022	368,122	46,761	0	1,357,000	293,335	0	0	6	3.6	4.2
S3	20.07.2022	572,686	68,430	0	1,856,000	289,905	0	6,060	17.2	3.4	4.7
S2	21.07.2022	369,308	45,283	0	1,299,000	228,305	0	0	0	0	0
S1	22.07.2022	374,414	45,239	0	1,399,000	297,995	0	0	0.4	1.6	2
	23.07.2022	367,200	44,867	0	1,175,000	277,230	0	0	0	0	0
	24.07.2022	354,197	45,286	0	1,160,000	274,755	0	0	0	0	0
S6	25.07.2022	357,530	43,537	0	1,241,000	271,170	0	0	0	0	0
S5	26.07.2022	314,463	42,402	0	1,236,000	248,605	0	0	0	0	0
M1	27.07.2022	379,123	43,018	0	1,377,000	93,980	0	0	0	0	0
S4	28.07.2022	351,145	42,661	0	1,157,000	257,880	0	0	0	0	0
	Sum	**4,879,107**	**602,145**	**0**	**16,722,000**	**3,407,835**	**0**	**6,060**	**24**	**9**	**11**
	Total sums	**25,278,397**	**3,109,849**	**9,393,541**	**77,537,000**	**14,018,936**	**1,296,554**	**1,215,230**	**143**	**109**	**51**

3.5 Limitations and opportunities

To complement previous studies in the Seine River on larger MPs (>80 and >300 µm) we used a novel stainless-steel pump filtration device to sample larger water volumes (up to one m^3) and at the same time extract smaller MPs. More recent studies employed the same sampling technique and even used the same instrument as part of a collaboration (Sefiloglu et al., 2024). With a small size cutoff (10µm) we experienced fast clogging of the filter mesh during MP sampling, seen as a negative relation between SSC and sampling volume (Figure SI 8). The device manual recommends to sample two runs until clogging for a representative MP sample. This led to sample volumes ranging largely (73-980L). More MPs are found in smaller sampling volumes (Cross et al., 2025) and our results confirm this trend, but the chance to sample rare MP types is lower. (Cross et al., 2025) developed a methodology to estimate representative sampling volume. Translating their principle to this study, we can make reliable statements on presence and absence of MPs (one particle needed), calculate sampling error (Poisson), achieve 95% confidence interval within 30% of total concentration (50 target particles) and evaluate MP properties like polymer type with a <5% error. To estimate size distributions with a small error it would need 620 particles. Particles per sample ranged from 7 to 707 (Table 2) in this study, so that we can confidently describe our data but with repercussions on the error sizes for simultaneous analysis of polymer type and size.

Samplings were conducted from the riverbank where water flow and river conditions may differ compared to the middle-section of the river and we did not access samples over the cross-section or in different depths along the water column, like other studies (Dris et al., 2015b; Erni-Cassola et al., 2024; Haberstroh et al., 2021). (Dris et al., 2024) calculated that the average number of sampling points in river studies was about ten. We sampled at six locations along the Seine and added a sampling location in an important confluence. However, we sampled each site four times, totaling 28 samples. The small sample sizes and the overall high data variations limit the statistical reliability of these findings. Our calculations of MP fluxes and mass fluxes assume that the measure MP concentrations are homogeneously distributed in the whole water column. Therefore, the flux estimations should be interpreted with caution and be used as guiding levels of the MP pollution load in the Seine River.

We investigated MPs in the Seine over a longer period, which is a recommended approach to better capture MP dynamics and assess site-specific factors. However, samplings were conducted on different days and although sampling campaigns were always within a two-weeks window, we experienced influences from local precipitation and variation in river flow rates (see also Figure 3). Heavier rainfall events and climatic dry periods have influenced the samplings in this study and hampered the clarity of the results to answer specific research questions regarding flow conditions. We recommend more attention to MP occurrence and fate in connection to climatic changes and extreme weather events, as those are becoming more frequent and intense (Calvin et al., 2023; Tabuchi et al., 2015).

We randomized the sampling based on personnel and material availability, but we highly recommend adjusting future sampling campaigns better to the river dynamics, e.g., sample upstream to downstream and sample sites close to each other in location and close in time. This could help to obtain data that is more relevant when comparing sites. Another study from our group (data not published) at sampling site S4 in 2022 showed high short-term variation during a

sampling. Due to the high variability in field samplings in general (Cross et al., 2025) we think improved monitoring design could minimize the temporal and spatial biases and increase the likelihood of measurements being more homogeneous. Temporarily, local boat traffic caused water movements and turbulence which led to sediment resuspension near our sampling device. To prevent a strong influence of this we stopped the sampling pump and continued when the sediments had settled. The Seine is a highly navigated river (Tabuchi et al., 2015, 2018). Future studies could target the impact of ship traffic on MP resuspension and dispersion. Also investigating point sources in a more targeted way and in combination with local samples can reveal MP release pathways into the Seine, as recommended by (Skalska et al., 2020). Future studies should include continuous measurement of MPs at relevant locations in the Seine, including covering the river cross section and vertical water column profile.

Limitation of the spectrometric methods used in this study to analyze MPs (µ-FTIR combined with siMPle particle identification) does not allow valid statements about particle shapes. While we refer to the polymer type, which is the best match for the plastic particle based on polymer libraries, we do not identify the complete chemical combination of the plastic, i.e., other polymers, composites, or additives. Information based on polymer chemical composition and particle shape differentiations could add to the depth of results and might give some first explanations for some of our observations. FTIR is one of the most applied method to analyze small MPs in freshwater studies (Gao et al., 2023) making our data comparable with other studies and complementing previous studies, extending on MP knowledge in the Seine River. Our study transparently details all data to assure reproducibility (Stratmann et al., 2024) and presents background information and secondary analyses in the SI section.

4 Conclusions and outlook

We assessed the upstream-downstream evolution of riverine MPs along the Seine River in four sampling campaigns in high-flow and low-flow river conditions. Insights from this one-year field study reveal that small MPs (25 - 300µm) are highly abundant in the upper water layer of the Seine River with three polymers dominating the contamination. PP, PE and PS are the dominant polymers, while minor polymers like ABS, PU, and SBR contribute less in terms of concentration, but their environmental impact remains relevant. Rural areas occasionally receive a varied mix of polymers, which shows the importance of understanding MP and plastic sources in the whole river catchment. The one-year monitoring of MP in the Seine River showed that the overall MP load increased from upstream to downstream, a result that was also found by others (Treilles et al., 2022). The unbalanced MP budget indicates MP retention and mobilization throughout and shows that, at times, MP may accumulate in the Greater Paris urban area and periodical MP transport downstream occurs. These results suggest that the MP dynamic from urban areas downstream is more complex. One-time measurements may not be reliable to draw a picture of a river's MP situation, and we recommend monitoring multiple urban and downstream locations regularly over time to better understand the MP emission, retention and transport in the river.

While MP concentration and flux in the Seine River both show positive correlation with river discharge, local factors and hydrological variability may be stronger than the influence of discharge on microplastic levels at individual sites and during certain conditions. The results strengthen the hypothesis that local and temporary conditions (e.g., MP emission or weather conditions) play a crucial role in explaining and understanding MP dynamics in the Seine, and

potentially in other rivers. The variability between campaigns and sampling sites indicates event-driven dynamics and we clearly see the effect of July and February precipitation on MP load. Other studies reported similar variability (Constant et al., 2020; Treilles et al., 2022).

We applied a mass balance and emission source tracking approach including a comprehensive description of MP levels and patterns at various locations and times related to wastewater discharge in Paris. The results of this study confirm the outcomes of previous studies that point at urban areas with limited sewage collection and treatment facilities as hotspots for MP contamination (Besseling et al., 2019; Koelmans et al., 2020; Schell et al., 2022). (González-Pleiter et al., 2021). Wastewater discharge is a common pathway for MP originating from households or industry application entering rivers (Dris, 2016; Enders et al., 2019; Nguyen et al., 2024; Rico et al., 2023). Understanding MP pollution in the Seine River in relation to sewer discharges is of importance as it provides a first basis for pollutant source flux and fate models. Such models help to develop pollutant control systems and mitigation measures, and to assess environmental impacts, one of the aims of the Parisian WWTP management (Tabuchi et al., 2018). The analyses in this study emphasize the substantial scale of MP contamination in the Seine River and the impact from urban discharges.

This study adds new data and quantifies the MP abundance and MP fluxes between 2021-2022. Many studies report MP abundance, i.e., MP concentration, but not MP fluxes or 'MP load' (de Carvalho et al., 2021; Devereux et al., 2023; Kunz et al., 2023; Leslie et al., 2017). In river systems, with a) directional movement of water masses, b) variable river discharge, driven by catchment hydrology (like rainfall, evaporation, drainage, seasons) and urban river management (e.g., sluices, reservoirs, diversion), and c) heterogeneous MP fate along the river through turbulences, punctual emitting sources, and more (Bai et al., 2022), considering the river flow is crucial. MP concentration at location in the river can be high, due to lower river flow in dry periods, but may get diluted during rainfall. Those dynamics are accounted for when MP fluxes are calculated, even though the underlining assumption is often a homogeneous distribution of MP particles throughout the water column.

Our findings suggested high variability and sinks of MP in the urban stretches of the Seine River which links to toxicity and environmental exposure. Toxicological studies test MP concentrations that often are magnitudes higher than concentrations measured in the field. However, with a steady accumulation of MP in certain river compartments it is likely to find locations with high concentrations (van Emmerik et al., 2022; Woodward et al., 2021). Assessing MP contamination in the Seine River is essential to understanding pollution levels and potential impacts on ecosystems and human health. Identifying sources, sinks, and transport pathways is key to effective MP mitigation and provides a basis for targeted future research. This research advances the understanding of contamination and fate of small MPs in rivers influenced by human activity. Further investigation into seasonal and environmental factors influencing these variations can provide insights helping shape targeted microplastic mitigation strategies.

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CHAPTER 5 METHOD COMPARISON FOR MICROPLASTIC SAMPLING IN RIVER WATER: *IN-SITU* PUMP FILTRATION VS. SETTLING TRAP (PAPER III)

Manuscript

Stratmann CN, Dris R, Gasperi J, Guerin S, and Tassin B *Method Comparison for Microplastic Sampling in River Water: In-situ Pump Filtration vs. Settling Trap* (2025)

Method Comparison for Microplastic Sampling in River Water: *In-situ* Pump Filtration vs. Settling Trap

Manuscript. The title is tentative.

Cleo N. Stratmann[1]* Rachid Dris[1] Johnny Gasperi[2] Sabrina Guerin[3] Bruno Tassin[1]

[1]Laboratoire Eau Environnement et Systèmes Urbains, École des Ponts ParisTech, Institut Polytechnique de Paris, Université Paris Est Créteil, Marne-la-Vallee, France
[2]Laboratoire Eau et Environnement GERS-LEE, Université Gustave Eiffel, Bouguenais, France
[3]Syndicat Interdépartemental pour l'Assainissement de l'Agglomération Parisienne (SIAAP), Paris, France

Highlights:

- *In-situ* variation is high: MP concentrations in both high-frequency pump (P) and sediment trap (ST) samples fluctuated strongly
- The methods have similar patterns of MP concentrations, but ST samples showed higher concentrations
- Detection of polymer types varied between both methods.
- PE and PP were the dominant polymers, consistently present in both sampling methods.
- Temporary occurrences of larger, denser polymers influenced the mass-based proportions, particularly in P samples.
- In P samples, MP particle size distributions were mostly consistent, with half of the particles [25–300 µm] under 100 µm; PE was more common among larger sizes, and PP among smaller ones.

Abstract

Most microplastic (MP) studies in rivers take samples at multiple sampling sites and often at different times or seasons, providing unique snapshots of MP data. Hereby two key factors are often disregarded: comparability with other studies and the reliability of the sampling method. This study determined and compared variation during sampling MP in a river water with a stainless-steel pump with *in-situ* cascade filtration (P), and a sediment trap (ST). MPs dispersion in the water column is inhomogeneous due to the diverse nature of MP particles and hydraulic conditions. High-frequency pump sampling with *in-situ* filtration was conducted to capture short-term variations in MP abundance, whereas the sediment trap allowed programmable long-term sample collection, potentially averaging out short-term fluctuations. Little knowledge is available about the *in-situ* variation of MP abundances during sampling. This study showed that polymer diversity, composition, and concentrations varied between sampling methods, while particle size distributions were consistent across samples and methods. Both methods showed similar MP concentration patterns, although ST samples generally exhibited higher concentrations. Temporary occurrences of denser polymers affected mass-based proportions, emphasizing the need to account for rare particle occurrences. There are ample inconsistencies between methods

used to sample riverine MPs, obscuring results and hampering comparability. This study acquired new knowledge of *in-situ* variation of methods and assessed a novel sampling method opening opportunities for MP monitoring.

1 Introduction

Microplastics are plastic particles in the µm size range (1 – 5,000 µm) (Hartmann et al., 2019) derived from direct production (primary MP) or by breakdown of larger plastics (secondary MP) (Thompson et al., 2024). Their negative impacts due to their persistence and chemical features have been studied and assessed throughout various environments including rivers. MP studies in the aquatic environment have increased tremendously in the past decade. SCOPUS search using the same keywords as Dris et al. (*Microplastic* AND *River*) and adjusting time of publication for after 2021 until present resulted in 2,353 articles, compared to 793 from 2018-2021 (Dris et al found 705 from 2018-2021) In total from 2013 until today this search resulted in 3,225 documents and the majority of articles are articles in the subject are Environmental Sciences (47%). This important scientific progress led to first estimates and insights into MP abundance and fate in different rivers around the globe (Scherer et al., 2020; Tan et al., 2023) and shaped MP modelling approaches (Akdogan & Guven, 2024; Besseling et al., 2017; Buschman et al., 2020; Kooi & Koelmans, 2019).

However, a wide array of sampling techniques was used throughout, hampering comparability across studies (Dris et al., 2024), a common pitfall complained about by many (Dris et al., 2024; Scherer et al., 2020). Large variation in MP levels are reported; (Scherer et al., 2020), for example, found that data from MP studies in European rivers ranged from 0.17 to 3.45 x 10^5 particles m^3. Even among studies MP concentrations can vary widely (Stratmann et al., 2024). The observed variation in MP concentration can be a natural phenomenon due to heterogeneous MP dispersion throughout the water column, MP release from sources, or MP mobilization, influenced by river hydrodynamics. Different analytical methods are also causing problems for comparability across studies and even replicates can exhibit large data ranges, showing that MP assessment from environmental samples is a difficult challenge (Becker, 2020; Ciornii et al., 2025; Dris et al., 2024; Elert et al., 2017; Sefiloglu et al., 2024; Song et al., 2015). The starting point of assessing variation though is sampling, as any error here multiplies throughout the rest of the analytical chain. The choice of sampling method is often based on multiple reasons, such as target MPs, availability, feasibility, cost, river compartment, or site conditions. Hereby, methods were invented and improved, and many studies aimed to contribute to harmonized sampling methods (Gerdts, 2019; Kittner et al., 2022; Rochman et al., 2017; United Nations Environment Programme, 2020). The reliability, LOD, and performance rate of a method itself needs to be assessed under controlled conditions like a calibration approach.

Another step toward standardization and improved data quality is the comparison of different sampling methods under real conditions. At the same time, assessing the potential temporal fluctuation in MP concentration during sampling is needed to distinguish methodological variation from environmental variation. Nonetheless, the evaluation of variation in MP concentration during sampling and the comparison of methods are still understudied. Previous studies concluded that higher sampling frequencies expose smaller-scale temporal fluctuation of MP concentration in rivers (Kukkola et al., 2024) and that a higher number of samples decreases uncertainty (Bruge et al., 2020). Comparison studies found that different methods result in differently biases MP data, under- or overestimating certain MP particles (Barrows et al., 2017; Hung et al., 2020; Karlsson et al., 2020; Kukkola et al., 2024; Pagter et al., 2018). In addition, studies assume homogenous concentration throughout the water column to extrapolate results, like annual MP flux in a river. But MPs dispersion in the water column is inhomogeneous due to the diverse nature of MP particles and hydraulic conditions and variation unknown and/or not reported.

The sampled MPs (sizes, polymer types, shapes) depend on sampling volume, method, and the number of observations (particles). But also, the environmental conditions affect the choice and performance of a sampling method. Net sampling is good to sample large water volumes, but this comes to the price of sampling larger particles, while pump sampling enables larger volumes and broader size range of particles. Grap samples can catch MP particles of all sizes but are usually small volumes due to logistical and filtration limitation (Dris et al., 2024; Hung et al., 2020; Watkins et al., 2021). Thus far, settling traps were only used to study settling MPs in a lake (Saarni et al., 2021, 2023; van der Deijl et al., 2017). This said, there is also an opportunity to use sampling methods complementary to each other to investigate MP more comprehensively.

To aid the understanding of variation in MP concentration and loads in river water during smaller timescales and to improve the knowledge of the comparability of sampling methods, this study presents a high-frequency and comparison sampling test in a French river. During five days of field samplings at the same location with repeated samples of MP in the upper water column (0.3-0.4 m depth) two methods were employed: a pump and a sediment trap.

a) Temporal fluctuations/variation in MP concentration and MP fluxes during field sampling with higher sampling frequencies in upper water column of a river using two methods: pump and sediment trap.
b) Comparison of two methods to sample MPs in the upper water column of a river.

2 Material and methods

2.1 Sampling site

Microplastic samples were collected at the sampling site, 'Bougival' (48°52'11.5"N, 2°07'45.8"E), a hydrological monitoring site in the Seine River operated by SIAAP (Figure 1). The site is situated

ca. 489 km downstream from the headwaters on the southern side of the Île de la Loge peninsula in the district Bougival, downstream of central Paris. The 750 km passage of the Seine River (annual mean discharge at Paris Austerlitz: 319 m^3s^{-1}) is impacted by agriculture and urbanization, particularly from Greater Paris, which has a population of over 12 million. Straightening, infrastructural changes and intensive river management have affected the course of the Seine. The sampling site is heavily influenced by urbanization, effluence of wastewater treatment plants (WWTP) Seine-Centre (SEC) ca. 12 km upstream, and two combined sewer overflow (CSO) locations (Clichy and La Briche) situated ~20 km upstream. The river flow of the Seine is characterized by summer (low) and winter (high) differences, but due to climatic changes the flow seasons are subject to changes. The Seine River splits into two sidearms ~10 km upstream of S4, and a lock for shipping is located just before the sampling location to connect the two sidearms. A small dam below bridge 'Pont abbe Peirre' located 360 m downstream of the site slows the water flow. Temporarily, a plastic gyre was observed in front of the dam (see Figure SI 1). The islands between the two river splits are vegetated. The riverside at the sampling site is vegetated with trees and plants. The riverbank slopes down to water depths of 3-4 m and is partly sandy with submerged vegetation. The water is reachable via a 5 m long pier with a water measurement station.

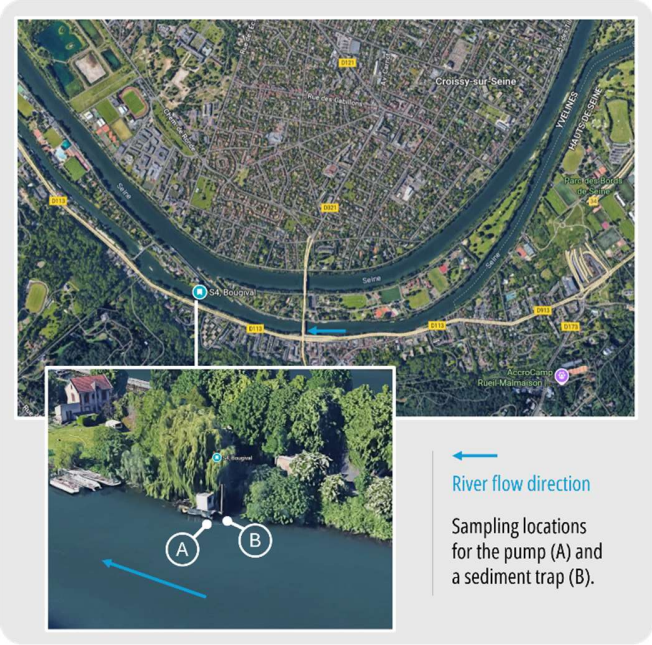

Figure 1 Sampling site and location 'Bougival'.

2.2 Sample collection

Samplings were conducted on five days in 2022: 21 February, 3–5 May and 28 July (Table 1). Thirty-four MP samples from the upper water column were collected using a pump (P, 24 samples) and a sediment trap (ST, 10 samples) at sampling locations A and B, respectively, ca. 1 m next to each other (Figure 2). ST and P devices were installed 30 cm below the water surface and ca. 1 m away from the pier, around 4 m from the riverbank. On three sampling days, multiple repeated samples were collected for both methods (P and ST). Samples were named using the format [month][day]-[method]-[# repeated sample]. In February, six pump samples (Feb21-P-1 to Feb21-P-6) and three sediment trap samples (Feb21-ST-1 to Feb21-ST-3) were collected. On 3 and 4 May, three pump samples per day were taken (May03-P-1 to May03-P-3; May04-P-1 to May04-P-3). On 5 May, six P and ST samples were taken in parallel (May05-P-1 to May05-P-6 and May05-ST-1 to May05-ST-6). ST samples were taken every full hour between 10:00 and 16:00 CEST, while P samples were taken at hourly intervals offset by 30 minutes, starting around 10:30 CEST (Table SI 1). Sample May05-ST-6 was lost during collection. In July, six pump samples (Jul28-P-1 to Jul28-P-6) and two sediment trap samples (Jul28-ST-1 to Jul28-ST-2) were collected. Samplings began between 10:00 and 12:55 European time and continued throughout the day (ending between 15:00 and 16:00 European time). In addition, basic physico-chemical water parameters were sampled on each sampling day.

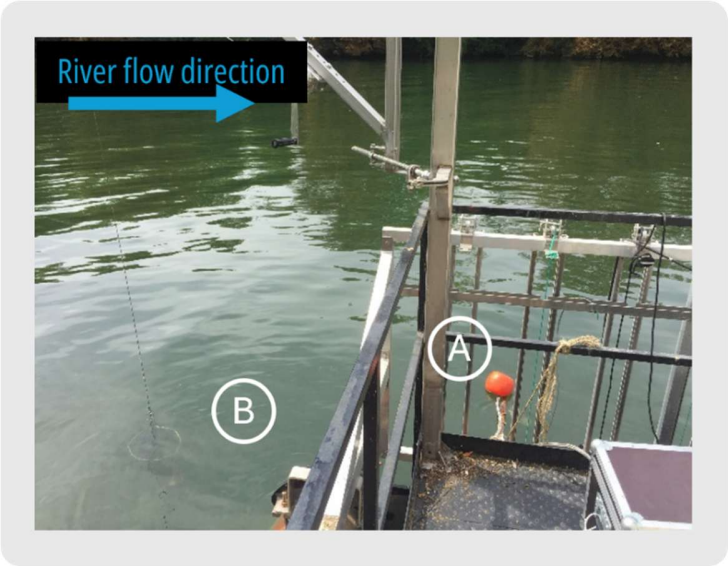

Figure 2 Sampling devices were installed at the end of the pier at sampling sites 'Bougival'. The pump (P) sampling inlet cage was 30 cm submerged in the water at point A and held in place with an orange plastic buoy fixed to a wooden stick. The sediment trap (ST) was also submerged with the opening at a depth of 30 cm, seen in this photograph at point B. The distance between the two devices was approximately one meter.

Table 3 Overview of samplings, local conditions and water parameters. P and ST samples were named: [month][day]-[method]-[# repeated sample]. ST samples marked with * could not be used in data analysis. River discharge (m3 s-1) at Paris Austerlitz, daily mean values.

Sampling date (dd-mm-YYY)	Pump samples (P)	P sampling volume (L)	Sediment trap samples (ST)	ST exposure time [min]	Local conditions	River discharge [m3/s]	Flow velocity [m/s]	Turbidity [[NTU]	Water temperature [°C]	Conductivity [µS/s]	SSC [mg DW/L]	pH -
21-02-2022	Feb21-P-1	61	Feb21-ST-1*	60	Windy, dry, cloudy	388	0.061	18.8	9.1	550	32.9	8.20
	Feb21-P-2	63.1	Feb21-ST-2*	-								
	Feb21-P3	64.5	Feb21-ST-3	30								
	Feb21-P-4	67.3										
	Feb21-P-5	58.6										
	Feb21-P-6	64										
03-05-2022	May03-P-1	91.2	-	-	Sunny, dry, no wind, cable work 20 m away	174	NA	3.5	18	583	3.19	8.13
	May03-P-2	90.8										
	May03-P-3	89.9										
04-05-2022	May04-P-1	92.6	-	-	Sunny, dry, no wind	169	0.012	3.4	18	561	3.35	8.15
	May04-P-2	87.6										
	May04-P-3	86.6										
05-05-2022	May05-P-1	84.1	May05-ST-1	60	Sunny, dry, no wind	169	-0.013	3.4	17.7	559	4.0	8.11
	May05-P-2	92.8	May05-ST-2	60								
	May05-P-3	87.8	May05-ST-3	60								
	May05-P-4	91.5	May05-ST-4	60								
	May05-P-5	74.9	May05-ST-5	60								
	May05-P-6	83.8	May05-ST-6*	-								
28-07-2022	Jul28-P-1	98.2	Jul28-ST-1	75	Sunny, dry, no wind	91	-0.013	4.2	24.5	572	8.4	7.55
	Jul28-P-2	156.5	Jul28-ST-2	75								
	Jul28-P-3	159.3										
	Jul28-P-4	168.7										
	Jul28-P-5	122										
	Jul28-P-6	146										

2.2.1 Pump sampling

Microplastics were sampled using a pump device developed by AAU in Denmark (Figure 3). An inlet cage with a mesh size of 5 cm was installed at a water depth of 30 cm and fixed in place using a wooden stick, natural fiber rope (sisal) and an orange plastic buoy. The inlet is connected to three filter units via a stainless-steel tube for two-stage filtration. Before sampling began, the pump was rinsed with 100 liters of river water at the sampling site, with no filters installed. Then, pre-muffled, 167 mm diameter, 300 µm and 10 µm stainless-steel filters were carefully and quickly placed into the filter holders using clean metal tweezers. The filter holders were then sealed with silicone rings and tightened to prevent leakage during sampling. River water was pumped onto the 300 µm filter and the filtrate passed over two parallel 10 µm stainless steel filters to capture MPs between 10 and 300 µm. The drainage water flowed back into the Seine, away from the inlet. Sampling continued until the 10 µm filters clogged, as indicated by a pressure increase of up to 1.8-2 bars, as measured by the pressure gauge. The sampling volume was measured with a water meter at the pump outlet. One sample consisted of the two 10 µm filters. Using clean metal tweezers, the two filters were carefully placed together, loaded sites facing together, in a clean 167 cm glass Petri dish. The Petri dish was wrapped in aluminum foil and then closed again to prevent any MP contamination. The samples were stored in a metal box in a cold, dark place (2–8 °C) until further processing. Two new 10 µm filters were placed into the filtration units as described above for the next sample. Sampling duration ranged from 10 to 28 minutes (Figure SI 2), and the sampling volumes were between 58.6 and 168.7 liters, with a median sampling flow rate of 5 L/min. When samples were time-coordinated with ST samples, pump sampling was paused and was restarted at the correct time for the next sample. All steel filters, aluminum foil and glassware used for sampling were pre-muffled at 550°C for two hours and otherwise cleaned with filtered tap water and ethanol (see also 1.2.1 Quality assessment and quality control).

2.2.2 Sediment trap samples

Microplastics were collected using a sediment trap (Hydrobios, H-444101) (Figure 3). The technical details of the device are presented in Table SI 2. Six clean 100 ml glass bottles (H-444151) were filled with 10 µm-filtered river water from the pump outlet (see 1.1.1) and screwed onto the underside of the sediment trap in the respective positions on the rotation plate (1-6). The trap was attached to a metal rope connected to a wrench and fixed to a metal arm at the pier. With the sample bottles in position, the sediment trap was moved into place and slowly lowered into the water with no samples blocking the end of the filtration funnel (starting position 0). The opening area (0.015 m^2) of the trap was lowered to a depth of 30 cm. Prior to this, the start time and automatic sampling duration (30, 60 or 75 minutes) were programmed using the OceanLab3 software (see also Figure SI 2). At the set time, the rotation plate moved to the next position (position 1 = sample 1, and so on) to capture sediment matter, including microplastics. After all

samples had been collected, the plate rotated back to the starting position (0) and the trap was moved to the pier. The bottles were carefully unscrewed and immediately covered with aluminum foil before being closed with a black LDPE lid. The samples were stored in the dark at 2–8 °C until further processing. The aluminum foil and all the glassware used for sampling were pre-muffled at 550°C for two hours and then cleaned with filtered tap water and ethanol (see also 1.2.1 Quality assessment and quality control).

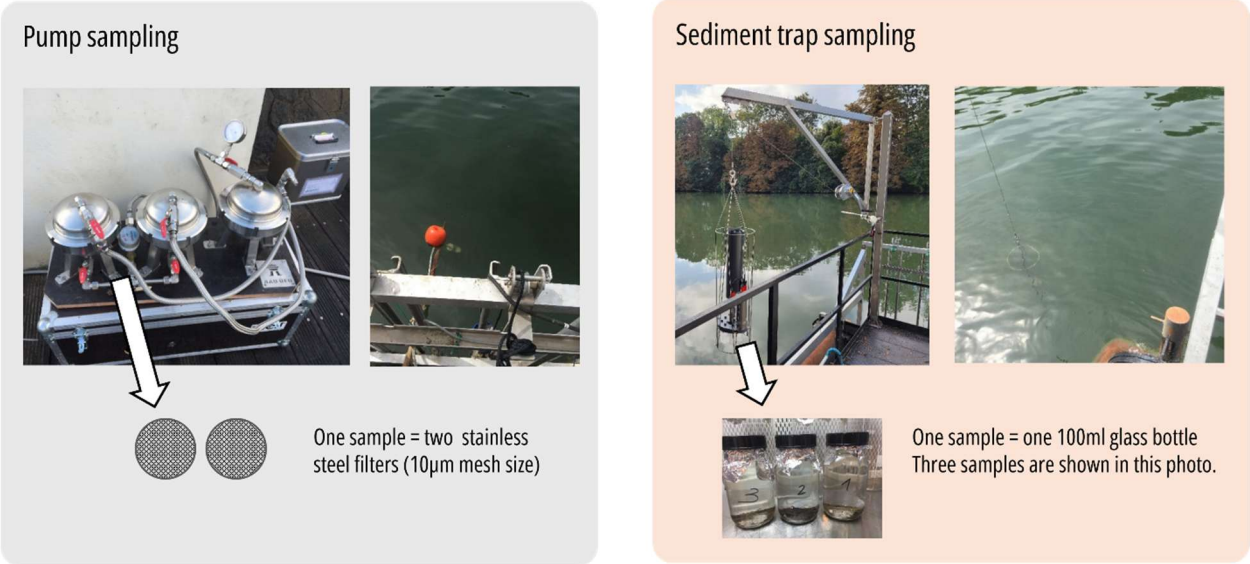

Figure 3 Sampling methods in comparison with the pump and *in-situ* filtration on the left side, and the sediment trap on the right side.

2.2.3 Physico-chemical water parameters

A clean, stainless steel 10-liter bucket was rinsed three times with river water from the upper water column, after which it was filled to around 5 L. Probe measurements for temperature, pH and conductivity were taken inside the bucket. Turbidity was measured using nephelometric turbidity units (NTU) in triplicate. This was done using an *in-situ* turbidity meter (Hach 2100P Turbidimeter). First, three turbidity standards were measured for calibration. Secondly, a clean 10 ml turbidity measurement glass tube was inserted upside down into the water in the bucket, which was homogenized by stirring. The tube was then turned to capture a homogenized subsample. The tube was then closed and dried with a clean towel on the outside before being measured. This process was repeated three times. The SSC was determined from a 1 L sample of river water taken with a clean 1 L glass bottle. The bottle was rinsed once with river water. The bottle was then held under the water, ca. 10 cm from the surface, and filled completely before being closed and stored in a dark, cold place (2–8 °C) until further treatment. The flow velocity at the specific sampling points (between A and B in Figure 2) was measured using a portable flow velocity meter (Flo-Mate 2000, Hach). Five replicate measurements were performed to capture the specific flow conditions. For turbidity and flow velocity, replicate measurements were averaged.

2.3 Sample analysis

2.3.1 Quality assessment and quality control

The processing of MP samples was done with precautions to prevent MP contamination of samples and to obtain the best results possible. Cotton lab coats and clothing made from natural fibers were always worn. Hands were washed with tab water and dried with natural cotton towels before laboratory work. All glass ware, filters, and where possible also metal equipment (including metal filters) was wrapped in aluminum foil and temperature treated at 550°C for 2 hours in a muffle oven. Where temperature treatment was not possible, equipment was washed and rinsed three times with filtered tab water (FTW) and filtered 95% ethanol (FE). Liquid solutions used in all processes for MP samples, i.e. tab water, ethanol, H_2O_2 and NaI solution were always filtered on a 2.7 µm pre-muffled GF/D filter. MP samples were always processed under a laminar flow bench and for the step of hydrogen peroxide treatment under the fume hood and workspaces were cleaned before each working step with FTW and FE. In addition, samples were always covered with pre-muffled aluminum foil. Plastic equipment was avoided throughout and only plastic rinsing bottles made from PTFE were used, as PTFE was not a polymer being analyzed with the software used in this study.

2.3.2 Microplastic sample processing

2.3.2.1 Pre-treatment of P samples

The steel filters were precut in 6-8 ‘cake’ pieces using a metal scissor and placed in a clean glass beaker. Each filter piece was rinsed inside the beaker with FTW, and water was filled up until all filter pieces were in solutions. The beaker was covered with aluminum foil and ultrasonicated (2-4 min).

2.3.2.2 Pre-treatment of ST samples

The ST sample was poured from the sample bottle onto an empty, pre-weighted (m_0) 10 µm stainless steel filter, using a standard glass-filtration unit. The bottle and the filtration funnel were rinsed three times with 2.7 µm-filtered tab water (FTW). The 10µm filter was transferred to a pre-muffled glass 47 mm petri dish using clean steel tweezers and wrapped in aluminum foil to prevent MP contamination. The joint ground flask of the filtration unit was replaced, and the filtrate (<10 µm) in the original ground joint flask was poured over a pre-weighted (m_0) GF/F filter (Whatman, 0.7 µm) using the same filtration setup. The bottle and filtration funnel were rinsed three times with FTW. The GF/F filter was removed with clean tweezers and stored in a clean petri-dish. The two petri dishes containing the 10 µm steel filter and the GF/F filter were then placed in the dry oven at 60 °C for >48 hours. The samples were then placed in the desiccator for at least one hour before weighing (m_1 and m_1). The sediment dry weight (DW) was calculated as the difference (Δm) between the dry weight of the loaded (m_1) and the empty filter (m_0) (Eq. 1).

$$\Delta m = \mathrm{m}_1 - \mathrm{m}_0 \quad \text{(Eq. 1)}$$

The total suspended sediment concentration (SSC_{total}) of ST samples was then calculated as the sum of the DW from both filters (m_S and m_{GFF}) (Eq. 2).

$$SSC_{total} = \Delta m_S + \Delta \mathrm{m}_{GFF} \quad \text{(Eq. 2)}$$

After weighing, the >10 µm sample fraction on the steel filter was resuspended in FTW via rinsing the filter three times followed by 2–3 minutes of ultrasonication with the filter inside the beaker. The sample was then treated alongside all other samples for MP analysis. The ST samples were treated without an upper size cut-off until the final stage of treatment.

2.3.2.3 Microplastic analysis of P and ST samples

MP sample analysis included organic matter removal by H_2O_2 wet-oxidation, inorganic matter removal by NaI density separation, and sample concentration on an anodisc filter for spectrometric analysis. H_2O_2 was added to each sample beaker so that a final H_2O_2 concentration of 10 % was reached. The beakers were covered with aluminum foil and placed in a shaking water bath at 30 °C for 18-24 hours. After wet-oxidation was done, for ST samples, the filter(s) were rinsed three times from each side, and a filter was placed into a glass-filtration unit, and the sample suspension was filtered on this. For P samples, the filter pieces in the beaker were discarded after rinsing three times, and a new 10 µm stainless-steel filter was used for the filtration step of the sample solution. Beaker and filtration funnel were rinsed three times with FTW. The loaded filters underwent resuspension with sodium-iodide (NaI) solution in the sample beaker (rinsed three times and 2-4 min ultrasonication). The NaI solution had a density between 1.63 - 1.7 g cm^{-3}. Then, the filters were rinsed into the beaker three times with NaI and removed to the petri-dish for storage. The NaI-sample suspension was now added into the JAMMS density separator units (Nakajima et al., 2019), filled up with NaI, and left for 18 - 24 hours. Then the upper part of the unit was recovered and filtered on a 10 µm filter from the petri-dish. The unit and the filtration funnel were rinsed three times with NaI, at the end three times rinsed with tap water to remove NaI traces. The loaded filter was then placed back into the glass beaker, and the filter underwent resuspension with FTW rinsing and ultrasonication. The ST samples were cascade filtered on 300µm and 10µm filter to split the size classes and the >300 µm fraction was stored separately. The 10 µm filter was then rinsed from both sites into the beaker with FTW and removed. The suspended sample was poured into an anodisc filter (diameter 25 mm, pore size 0.2 µm, Whatman), and the beaker and the funnel were rinsed three times with FTW. The anodisc filter was carefully recovered and stored in a clean glass petri-dish at room temperature for micro-Fourier-transform infrared spectroscopy (µ-FTIR) analysis.

During the laboratory treatment, sample solutions were filtered on 10 µm pore sized stainless steel filters with a diameter of 47 mm. To resuspend samples between the

processing steps filters were rinsed three times into the respective glass beaker with FTW or the appropriate solution and underwent 2- 4 minutes of ultrasonication. Glass beakers were always covered with pre-muffled aluminum foil during all procedures. During the procedures, the filters were stored in clean glass Petri dishes at room temperature.

2.3.3 Spectrometric microplastic analysis with µ-FTIR

Polymer types and characteristics of the MP particles were assessed by spectrometry. Spectra for all particle on the anodisc filter (100% of the sample) were obtained by automatic µ-FTIR imaging mapping the whole filter area. We obtained absorbance spectra in transmission mode using the KBr imaging detector and a short collection time (1 scan) with a spectral resolution of 8. We used the Nicolet iN10 (Thermofisher) µ-FTIR spectrometer with 16 detectors of 25 µm x 25 µm cells and microscopic zoom resolution of 400 x 500 µm. The detector cell size (25 µm) defines the lower limit for the size of the MP particles (effective final resolution). The detectors spectral range is comprised between 4'000 cm^{-1} – 1200 cm^{-1}. The transmission signal was filtered using Harris-Blackman method and was autobaseline-corrected. A background spectrum was taken before sample measurement from a clean, empty anodisc filter.

2.3.4 Particle analysis with siMPle

Spectra were evaluated using systematic identification of MP in the environment software (siMPle® v 1.1.β) (Liu, F. et al., 2019; Primpke, S. et al., 2019). Spectra from the particles were compared to reference spectra to identify the polymer type with the best matching score using a two-probability threshold. The software also provided particle characteristics such as particle dimensions, volume, and mass. The algorithm built into siMPle assumed an ellipsoid particle shape and a thickness of 0.67 × minor particle dimension to estimate the particle volume. Particle mass was then calculated as volume × polymer density.

2.3.5 Suspended sediment concentration analysis

The standard procedure for the determination of SSC (ASTM D3977) was followed with one slight modification: the drying process was at a temperature of 60°C for minimum 48 hours. The entire SSC water sample was weighted full, and the content was then filtered on a pre-weighted and muffled GF/F filter (pore size 0.7 µm, Whatman). The bottle was rinsed three times with FTW and then weighted empty to determine the exact sample volume. The filter was placed in a petri-dish and dried at 60C for >48 hours, desiccated (minimum one hour) and weighed again (m1). Calculation of DW on the filters was done according to (Eq. 1). SSC [mg L^{-1}] was then calculated as the DW per sample volume V_S. V_S was hereby determined as the difference between the full and empty sample bottle.

$$\mathrm{SSC} = \frac{\Delta \mathrm{m}}{V_S} \quad \text{(Eq. 3)}$$

2.4 Data analysis

Data analysis was conducted using Microsoft excel and R version 3.4.3.3 (R Core Team, 2021). We followed a protocol to assess the data before applying statistical tests (Zuur et al., 2010). One sample (Feb-2022-ST1) was removed from analysis as the sample seemed contaminated which was confirmed by re-evaluation of the filter used for FTIR analysis. For pump samples (P), MP concentration was calculated as number of MP particles (N [#]) or mass of MP particles (mass) per sampling volume V_S (Eq. 1-2).

$$MP\ concentration\ [\#\ L^{-1}] = \frac{\text{N [\#]}}{V_S\ \text{[L]}} \quad \text{(Eq. 4)}$$

$$MP\ mass\ concentration\ \ [\mu g\ \text{m}^{-3}] = \frac{\text{MP mass [ng]}}{V_S\ \text{[L]}} \quad \text{(Eq. 5)}$$

The MP concentration of P and ST samples was calculated per DW of suspended sediments (SS) in the water phase or for the sediment trap, respectively. SS concentration in the water was calculated as the difference between loaded (m_1) and empty weight (m_0) of the GFF-filters per filtered volume.

$$MP\ concentration\ [\#\ \text{g}^{-1}\ DW] = \frac{\text{N [\#]}}{\mathbf{V_S}\text{[L]} \times \text{SSC [g DW/L]}} \quad \text{(Eq. 6)}$$

$$MP\ concentration\ [\mu g\ \text{g}^{-1}\ DW] = \frac{\text{MP mass [g]}}{\text{V}_S\text{[L]} \times \text{SSC [g DW/L]}} \quad \text{(Eq. 7)}$$

The DW of sediments was determined for ST samples in May and July 2022. The DW was used to obtain sediment accumulation rate (SAR) (Eq. 5). The SSC per sample ($SSC_{total,i}$) was divided by the opening area of the sediment trap cylinder (A_{ST}), which was 0.015 m^2, and the sampling time (t_i).

$$SAR_i\ [g\ m^{-2}\ day^{-1}] = \frac{\text{SSC}_{total,i}\ \text{[g]}}{A_{ST}[\text{m}^2] \times \text{t}_i\ \text{[min]}} \times 1440 \quad \text{(Eq. 8)}$$

For all sediment trap samples (ST), the MP vertical flux rate (VFR) was calculated as number or mass of MP particles per square meter and day (Eq. 3-4). The number of particles was divided by A_{ST} and t_i. A time conversion factor of 24 was multiplied to obtain the rate per day. This unit was used to compare ST samples from February and July with May samples, as at those two campaigns, the SSC was not determined.

$$VFR_i\ \ [\#\ m^{-2}\ day^{-1}] = \frac{\text{N [\#]}}{A_{ST}[\text{m}^2] \times \text{t}_i\ \text{[min]}} \times 1440 \quad \text{(Eq. 9)}$$

$$\text{VFR}_i\ [\mu g\ m^{-2}\ day^{-1}] = \frac{\text{MP mass } [\mu g]}{A_{ST}[\text{m}^2] \times \text{t}_i\ \text{[hr]}} \times 24 \quad \text{(Eq. 10)}$$

Descriptive statistical metrics, including the median, interquartile range (IQR) and range (min – max), were calculated for each sample. Variation among samples of the same sampling methods was assessed using the relative differences (%) calculated as (max-min)/min*100. Paired comparisons (e.g. P vs. ST) were analyzed using the Wilcoxon

signed-rank test. Comparisons among two groups were conducted with the Mann-Whitney U test, and among more than two groups the Kruskal-Wallis test was applied. Statistical significance was assessed at a threshold of $p < 0.05$.

3 Results

3.1 Sampling conditions

Weather conditions were windy and dry in February, and calm and dry in May and July with water temperatures ranging between 9.1 °C in February and 24.5 °C in July. Turbidity was highest in February (18.8 NTU) and lower in May and July (3.4 - 4.2 NTU). Conductivity at 25°C was stable across all sampling days (550–583 µS s^{-1}), and pH values ranged from 7.55 in July to 8.20 in February. Daily river discharge, measured at Paris Austerlitz hydro station, was highest in February (288 m^3 s^{-1}). Daily river discharge in May was similar on all three days (~170 m^3 s^{-1}) and was low in July (91 m^3 s^{-1}). As expected, the flow conditions at the sampling points close to the shore were very calm. The flow velocity measurements available for four of the five sampling days were low and fluctuated, sometimes in the negative range, but were within the instruments' LOD (range: -0.15 – 6 m^3 s^{-1}) (Figure SI 4). Regularly observed backflow was confirmed by the flow velocity measurements. SSC in the water column was higher in February (32.9 mg L^{-1}), followed by July (8.4 mg L^{-1}) and was stable over the three days in May (~3.2-4.0 mg L^{-1}). Scatterplots of SSC versus Turbidity and versus river discharge show linear relationships (Figure SI 5). Due to small number of data points (N=5), further tests are not meaningful.

3.2 Pump samples

3.2.1 MP concentrations and polymer types

MP concentrations for all samples during the five sampling days are summarized in Table 2 and presented in detail in Table SI 3. Sample May05-P-3 contained only one particle. The median MP concentration for P samples was highest in February, followed by July and May, and differences across the three campaigns were found between February – May (Kruskall-Wallis, $p<0.01$) and May – July ($p=0.01$) (Figure 4). MP concentrations fluctuated during each sampling day, but mostly in February. For February, the MP concentration of the six samples ranged from 0.36 to 3.18 # L^{-1}. During the three consecutive days in May, MP concentrations were of the same order of magnitude with medians of 0.15, 0.16 and 0.26 # L^{-1}, respectively. Among the May samplings, the range of concentration was highest on 5 May, and the relative variation was high. In July, MP concentrations ranged between 0.37 and 1.28 # L^{-1} (median: 0.62 # L^{-1}). The mass concentrations show the same pattern with highest median concentrations in February (1,096 ng L^{-1}), followed by July (157 ng/L) and the three May samples (11, 18, and 41 ng L^{-1}, respectively). Mass and number concentrations correlate overall (Spearman's

rho=0.92, p<0.01), but the direction of correlations were slightly different across the days (Figure SI 6).

Table 2 MP concentration statistics / variation, relative variation as: (Max-Min)/Min)*100%

Campaign	Method	Median [# L^{-1}]	Min – Max (Range) [# L^{-1}]	IQR	IQR (25%)	IQR (75%)	Relative variation
February (N=6)	P	1.83	0.36-3-2 (2.8)	1.90	0.89	2.79	778%
May all (N=12)	P	0.16	0.01-0.4 (0.39)	0.15	0.14	0.29	3,900%
May 03 (N=3)	*P*	*0.15*	*0.09-0.17 (0.08)*	*0.04*	*0.12*	*0.16*	*89%*
May 04 (N=3)	*P*	*0.16*	*0.16-0.29 (0.13)*	*0.6*	*0.16*	*0.22*	*81%*
May 05 (N=6)	*P*	*0.26*	*0.01-0.4 (0.39)*	*0.17*	*0.12*	*0.29*	*3,900%*
July (N=6)	P	0.62	0.37-1.28 (0.91)	0.54	0.39	0.94	245%

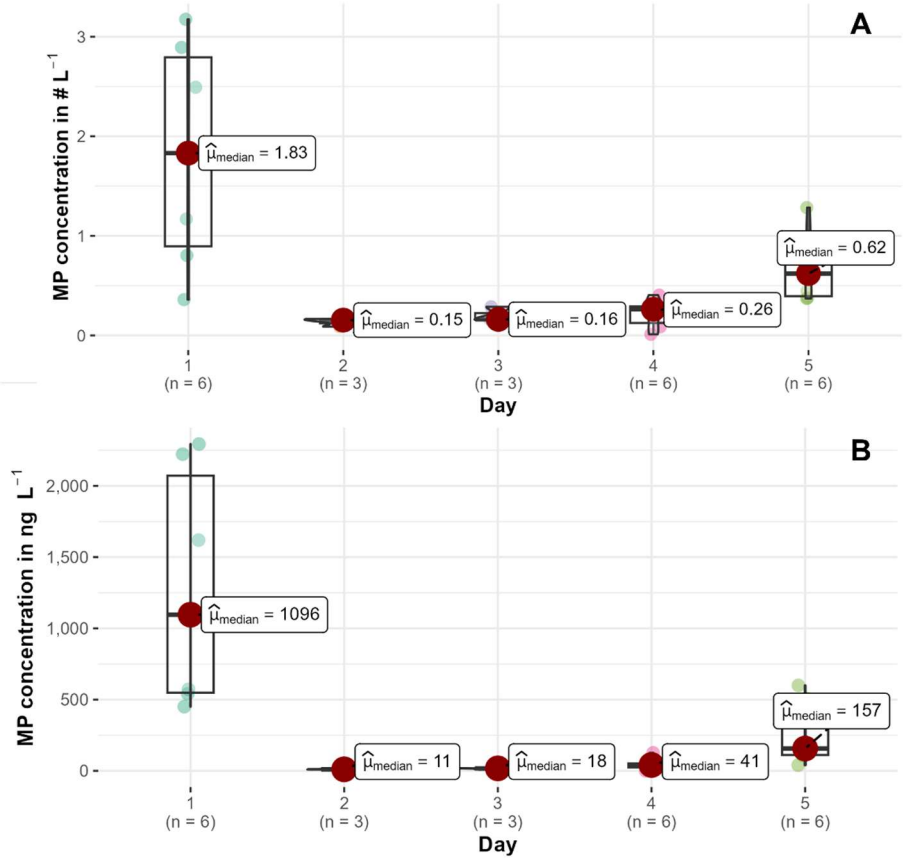

Figure 4 MP concentrations of pump samples across the sampling days 1 = 21 February, 2 – 4 = 3, 4, and 5 May, 5 = 28 July.

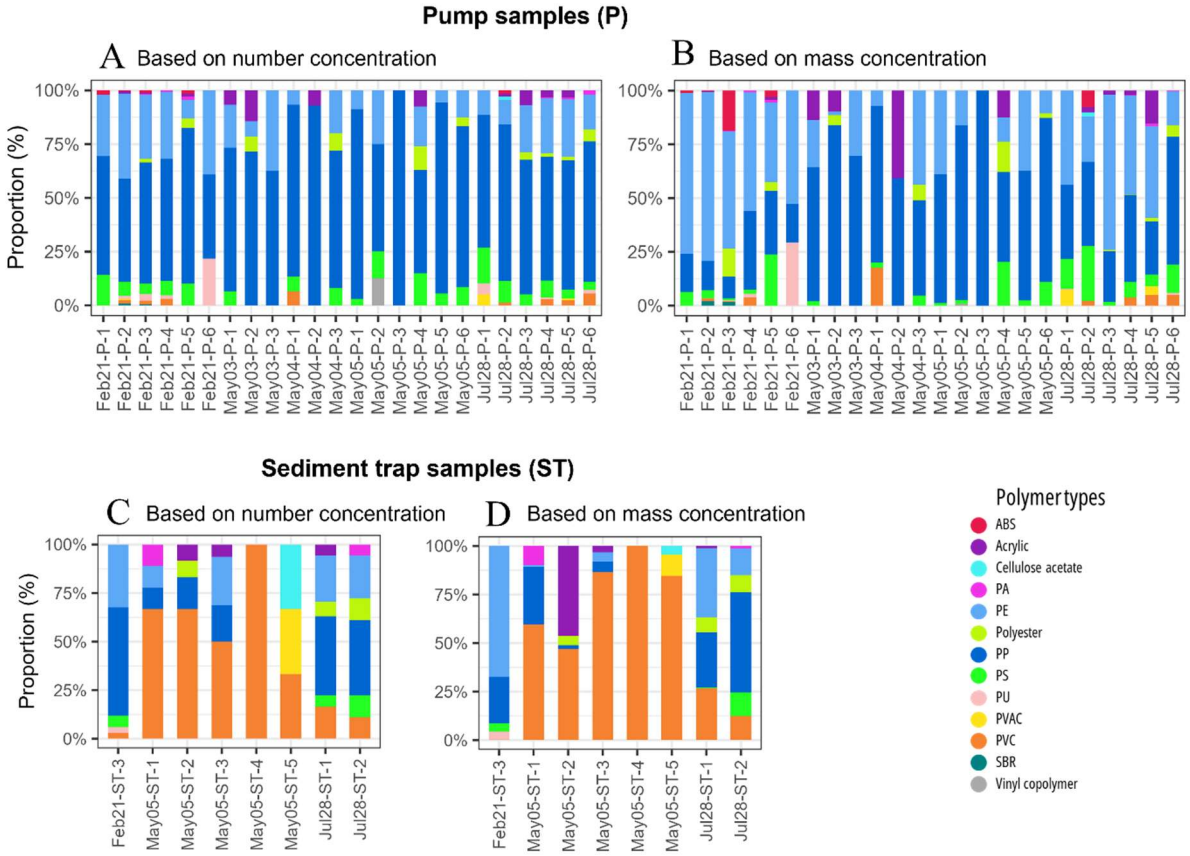

Figure 5 Proportions of polymer types for each pump (P) and sediment trap (ST) sample calculated from number concentration (A, C) and mass concentration (B, D).

3.2.2 MP sizes

Half of all MP particles in P samples were between 25 and 100 µm (47%), 35% were between 100 and 200 µm, 10% between 200 and 300 µm, and 8% were larger than 300 µm (Figure 6 A). When the size composition was based on the MP mass concentrations, the reverse pattern was found, with most of the mass at the larger size classes. The relation of minor to major particle diameter was consistent overall (Figure SI 9) and throughout the sampling days, independent of the range of dimension (Figure 7). But the particle sizes and the size distributions varied across samples (Table SI 3, Figure 6 B). In most February and July samples, half of the MPs were in the 25-100 µm size class. Only sample Feb21-STP6 had a higher proportion of large particles (>300 µm: 26%) and a smaller proportion of 25-100 µm-sized particles (26%). The number of observations in this sample was smaller (N=23) compared to other samples (N=49 to 200) during the February campaign. In May, the proportion of smaller particles was higher (for all May samples: 68%) and only a small proportion of MPs was large. Two samples contained particles above 300µm (May05-P-1 and 6), and six samples contained MPs in the >200-300 µm range. However, the number of observations per sample were smaller in May (N=1 to 34). The six July samples (N=55 to 217) seem

homogeneous containing MPs in all size classes, but the proportions of small particles are lower in some of the samples.

When aggregated by sample, the distribution of polymer types across size classes was uneven. The dominant polymers, PE and PP, displayed a reverse pattern, with PE particles being more prevalent in the larger size classes and PP in the smaller ones. However, polymer types such as ABS, PU or SBR, for which there were only few observations, were found across different size classes.

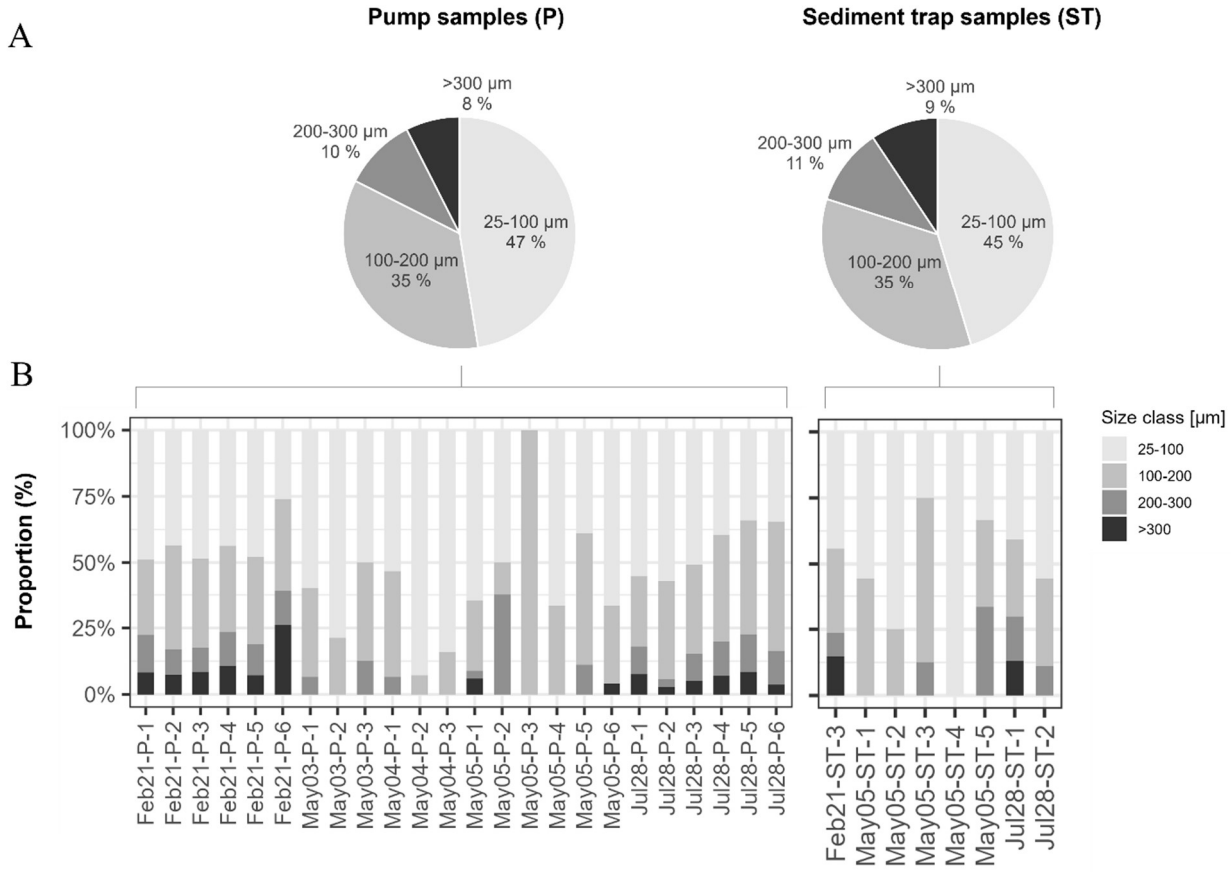

Figure 6 A) Pie charts showing the proportion of MPs per size class based on major particle diameter (25-100, >100-200, >200-300, >300) for all pump samples (P) and sediment trap samples (ST). B) Proportions of microplastics per size class (based on major particle diameter) for each sample. For P samples, bars are weighted by MP concentration (# L^{-1}); for ST samples, by VFR (# m^{-2} day^{-1}).

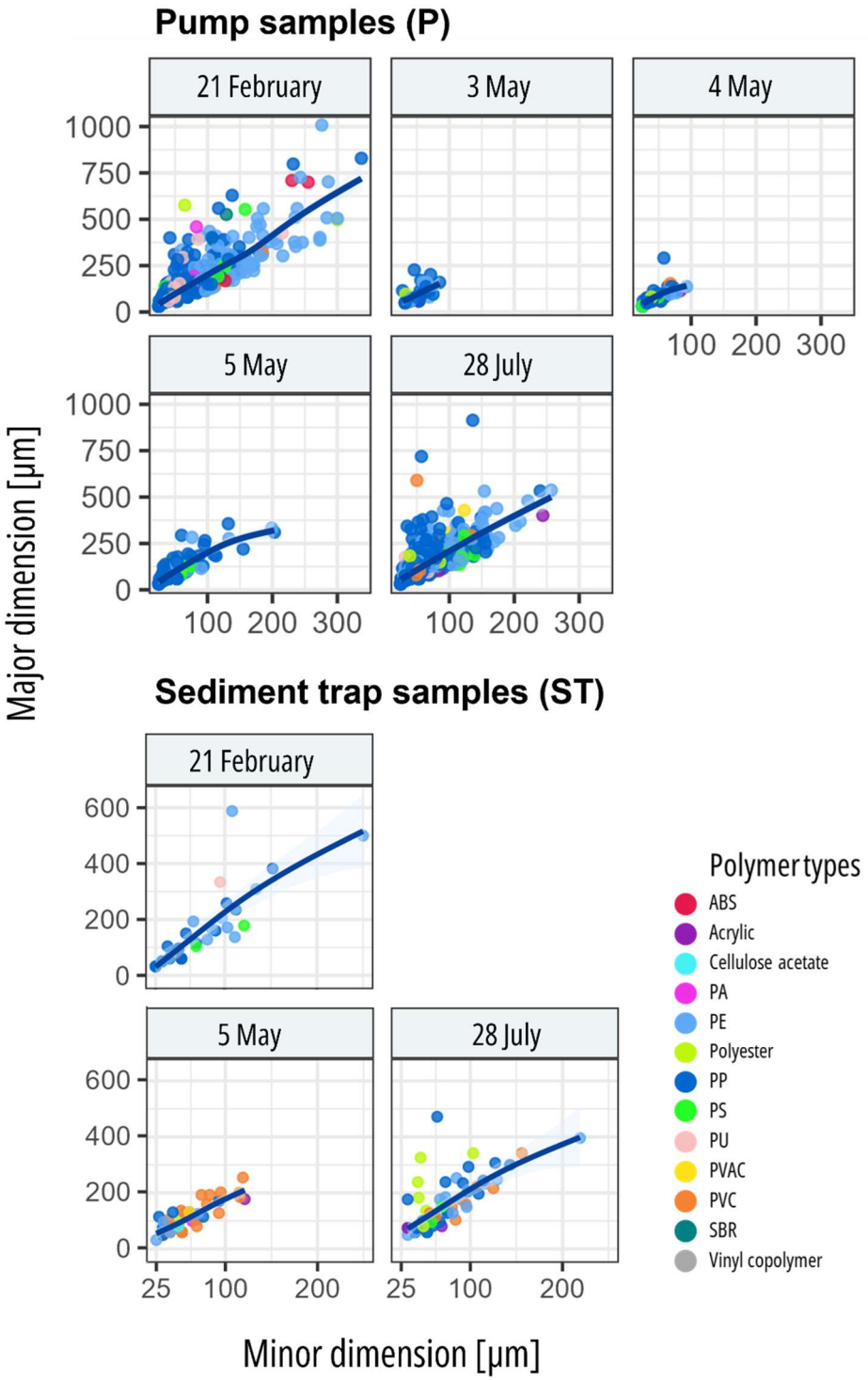

Figure 7 MP size distribution of all P samples, displayed in panels per sampling day (1 = 21 July, 2 = 3 May, 3 = 4 May, 4 = 5 May, 5 = 28 July). The number observations per sampling day: N=696 on 21 February, N=37, N=54, and N=112 on the three consecutive days in May, and N=599 on 28 February.

3.3 Sediment trap

3.3.1 MP concentrations

The MP vertical flux rate (VFR) was calculated for all eight ST samples and ranged between 1.6× 10^3 and 108×10^3 # m^2 day^{-1} (261-73×10^3 µg m^2 day^{-1}) (Figure 8). The highest median VFR was observed in February, followed by July and May. The same pattern across the campaigns was observed for P samples (see also 2.2.1). The MP concentrations per suspended sediment and the SAR were calculated for the five high-frequency samples on 5 May only (Table 3, Figure 9). MP concentrations ranged between 172 and 3,333 # g^{-1} DW (median: 2,500 # g^{-1} DW) with respective mass concentrations ranging between 28 and 1,112 µg g^{-1} DW (median: 434 µg g^{-1} DW) (Table 3). A strong correlation between VFR and MP concentration was observed (rho=0.90, p=0.04) (Figure SI 11). MP concentrations fluctuated between samples from the same day. The SAR for samples on 5 May ranged from 4.4 to 13.4 g DW m^{-2} day^{-1}.

Table 3 MP metrics for ST samples

Sample	MP concentration [# g^{-1} DW]	MP mass concentration [µg g^{-1} DW]	MP vertical flux rate (VFR) [#m^{-2} day^{-1}]	MP vertical mass flux rate (VFR) [µg m^{-2} day^{-1}]	Sediment accumulation rate (SAR) [g m^{-2} day^{-1}]	Median major particle diameter [µm]
Feb21-ST-3	-	-	108,800	73,795	-	110
May05-ST-1	3,214	532	14,400	2,386	4,4	81
May05-ST-2	2,500	434	19,200	3,331	7.7	78
May05-ST-3	3,333	1,112	25,600	8,541	7.7	127
May05-ST-4	172	28	1,600	261	9.3	81
May05-ST-5	357	214	4,800	2,877	13.4	131
Jul28-ST-1	-	-	69,120	36,302	-	133
Jul28-ST-2	-	-	23,040	3,588	-	89

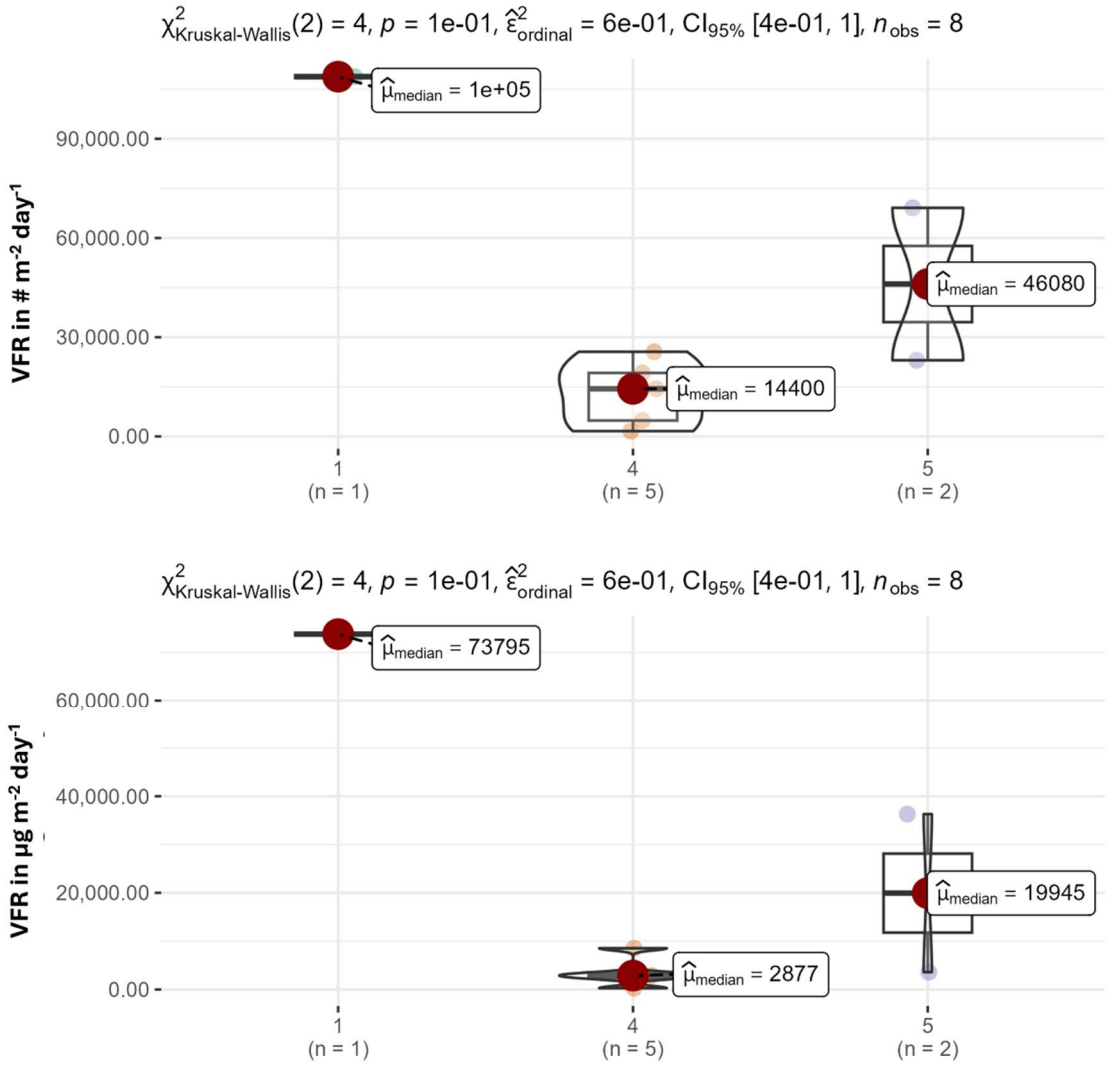

Figure 8 ST MP vertical flux rates (VFR) over the three sampling days.

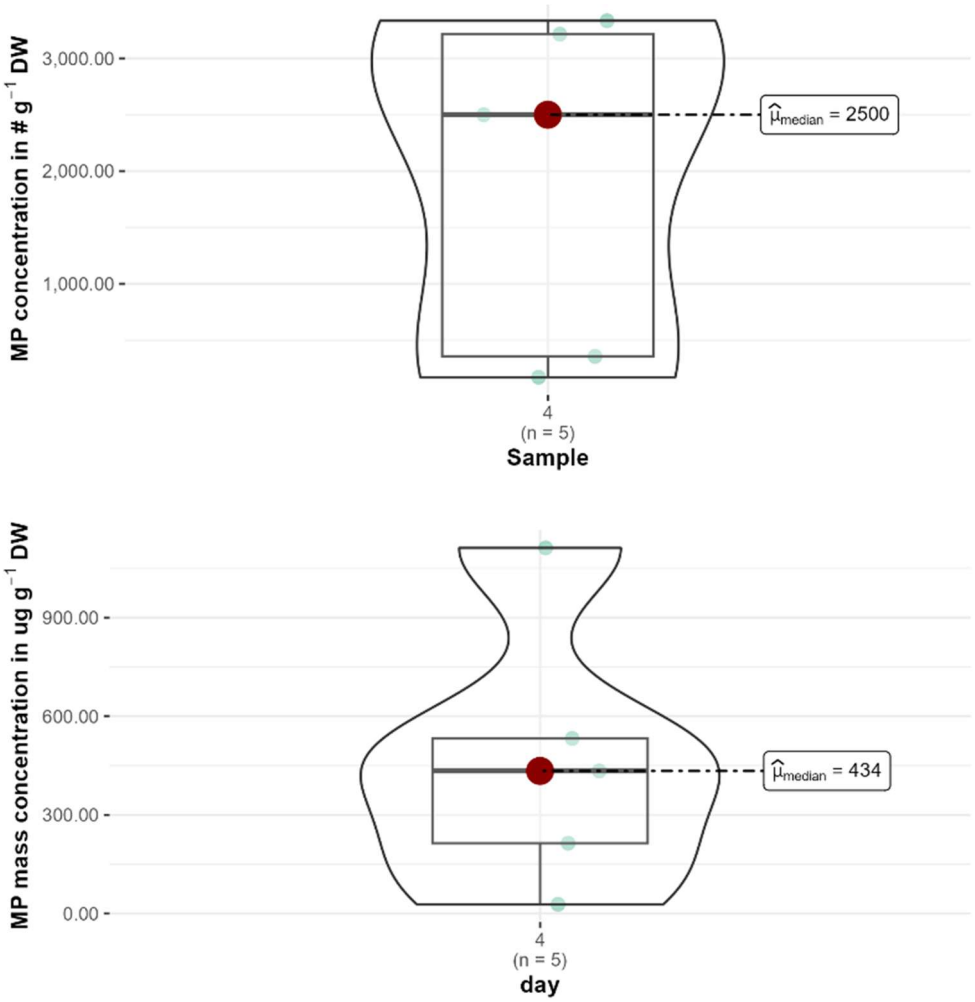

Figure 9 MP concentration and mass concentration for ST samples on 5 May 2022.

3.3.2 MP sizes

The MP particle size distribution of ST samples overall is comparable to P samples (Figure 6 A). This overall distribution holds representative for ST samples in July and February, with slightly larger MPs in February (>300 µm: 15%). In May, most MPs were 25-100 µm (49%) and >100200 µm (44%), but no MPs >300 µm were found. The size composition fluctuated across the high-frequency samples in May (Figure 6 B). The proportion in size classes based on number and mass gave a reverse relationship same as for P samples, with small particles making most numbers, but less of the mass.

3.4 Method comparison

Consistent patterns of MP metrics (concentration ~VFR) were observed, indicating that both methods capture a similar MP situation in the water column. MP concentrations for P samples and MP flux rates showed a similar pattern across the three sampling campaigns (compare Figure 4 and Figure 8). More specifically, the MP concentrations

per SSC were compared for P and ST samples from the sampling day 5 May. The median MP concentrations was much higher in ST compared to P samples (Table 4, Figure 10). However, ST samples contain less observations (N, number of particles detected) (Table 5). This is a common observation that fewer particles detection led to higher MP concentration estimations (an potential overestimation). Distinct differences in polymer type composition between P and ST samplings were detected (Figure 5). A smaller variety of polymer type was detected in ST samples (Table 6). To test whether the presence of polymer types differed between the two methods (P and ST), we compared presence and absence data and applied Fisher's exact test. PS was more frequently detected in the ST than the P samples ($p < 0.05$) (Table SI 7). PVC was only present in ST samples but not in P samples of 5 May. Polymers that were never detected across replicates were excluded from statistical testing. When comparing the relative polymer composition in the samples (only for polymers that were present on 5 May samples of both methods) across both methods, PP was more prevalent in P samples (Wilcoxon rank-sum test, p=0.02).

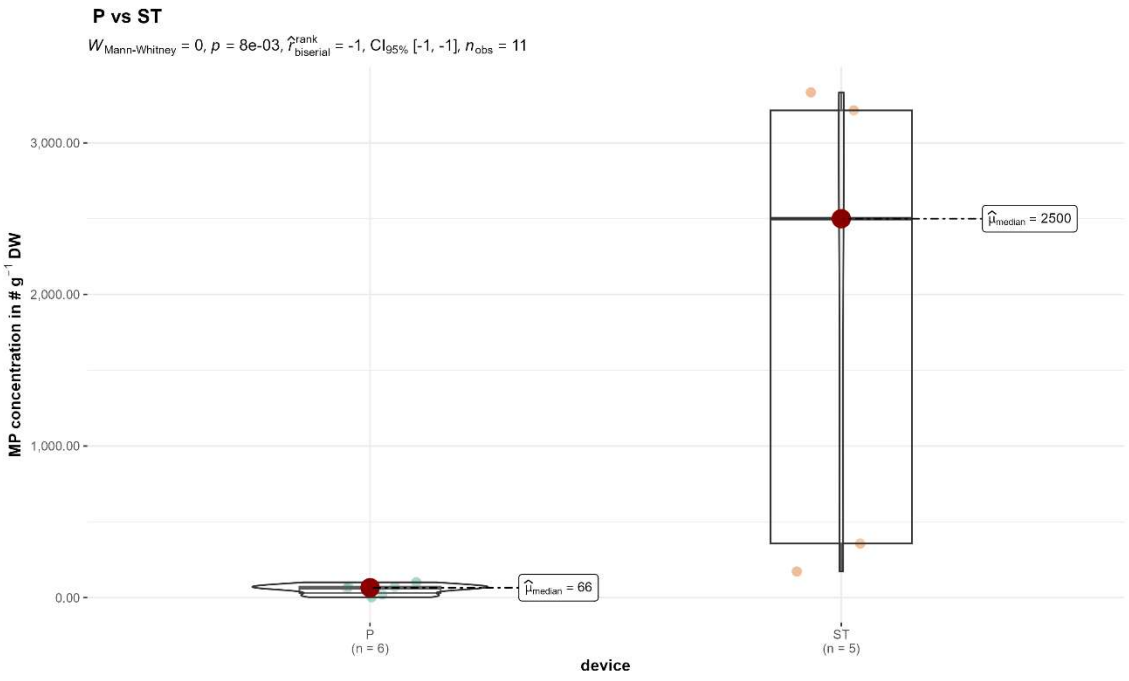

Figure 10 MP concentrations per SS for P versus ST samples on 5 May 2022.

Table 4 MP concentrations and particle metrics for ST and P samples on 5 May

Campaign	Sample nr.	MP concentration [# / g DW]		MP mass concentration [µg / g DW]		Median particle mass [ng]		Median particle size [µm]	
		P (N=112)	ST (N=41)	P	ST	P	ST	P	ST
May	1	101 (N=34)	3,214 (N=9)	32	28	37	53	81	81
May	2	22 (N=8)	2,500 (N=12)	8	434	107	71	117	78
May	3	3 (N=1)	3,333 (N=16)	0	1,112	45	175	104	127
May	4	73 (N=27)	172 (N=1)	6	28	58	163	81	81
May	5	60 (N=18)	357 (N=3)	13	214	65	196	120	131
May	6	71 (N=24)	-	13	-	54	-	81	-
Relative variation:		24,554%	4,659%	3,462%	2,263%				

Table 5 Data overview, N, and MP size metrics for P and ST compared by campaign.

Campaign	Method	N (particles detected)	Median major particle diameter [µm]	Maximum major particle diameter [µm]	Median particle mass [ng]
February	P	696	104	1008	114
February	ST	34	110	588	157
May	P	203	81	356	50
May	ST	41	100	255	83
July	P	599	104	914	97
July	ST	72	115	472	140

Table 6 From a total of 13 different polymer types, the detection frequencies are presented aggregated over sampling campaign and sampling method (pump – P, sediment trap – ST).

Campaign (day)	Method	Detection frequency	Polymer types
February (day 1)	P	11	PE, PP, PS, PVC, ABS, Acrylic, PA, Polyester, PU, PVAC, SBR
	ST	5	PE, PP, PS, PVC, PU
May (day 2)	P	5	PE, PP, PS, Acrylic, Polyester,
May (day 3)	P	6	PE, PP, PS, PVC, Acrylic, Polyester
May (day 4)	P	6	PE, PP, PS, Acrylic, Polyester, Vinyl copolymer
	ST	8	PE, PP, PVC, Acrylic, Cellulose acetate, PA, Polyester, PVAC
July (day 5)	P	11	PE, PP, PS, PVC, ABS, Acrylic, Cellulose acetate, PA, Polyester, PU, PVAC
	ST	7	PE, PP, PS, PVC, Acrylic, PA, Polyester

4 Discussion

The fluctuations of MP concentrations of P samples indicate strong variability between the samples in each campaign. The size distribution of MPs was more consistent within sampling campaigns when the number of observations of samples was larger. The results indicate that the number of observations in February and July (median N=118 and N=74, respectively) was sufficient in terms of size evaluation of MPs. A comparable size composition was found within both campaigns. One sample with enough observations is likely to be representative for the MPs size composition in the Seine River, when sampling with the pump device used in this study. Interestingly, the composition was similar not only within a campaign but also when comparing February and July. This further indicated that the MP sizes in the Seine upper water columns could be consistent throughout. The observation of consistent MP particle sizes in the Seine River was also made in an earlier study, which compared MPs [25-300 µm] from upstream to downstream of Paris and includes the February and July data used here.

The duration of samplings was similar for all P samples, but sampling volumes differed slightly and could be an explanation for the variation in the observed MP sizes. Also, true fluctuations can be part of the explanation. The small number of observations distorts the analysis throughout the size classes, and it is not possible to generalize the results. The results for the May campaign suggest that the number of observations (median N=15 per sample) was not sufficient, as the size composition per sample fluctuated. But to enhance the accuracy of results from MP measurement and the comparability across studies better understanding of the methodological and local intricacies is needed. Variation was observed among high-frequency samples of the same method, indicating that snapshot sampling results should be interpreted with caution. High-frequency sampling or taking replicates as recommended by others (Bruge et al., 2020) is therefore essential to better capture temporal variability instead of relying on single, large-volume samples.

5 Conclusion

The aim of this study was to better understand the variation of MP concentration in high-frequency sampling. A pump sampling device with direct *in-situ* MP cascade-filtration was used to sample MP 25-300µm. MP are not homogeneously distributed throughout the water column in a river and understanding the *in-situ* variation during sampling is important for reliability of results. The variation during field sampling in rivers has not been researched extensively yet. Methods to sample MP concentration vary across studies and within studies, making comparison of data and the right choice of method more difficult. While studies often get compared, it is important to understand the differences as this determines the results. The ST and P, both methods consistently captured MPs and similar patterns were observed, which indicates comparability of trends between the methods. However, the results were not in the exact same units and could not be perfectly compared. Substantial variability exists within and between

methods. ST tends to capture fewer particles despite exposure time being longer than P sampling duration, and more heavier polymer types. Method choice critically affects results, so MP data should always be contextualized with method uncertainty.

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CHAPTER 6 SYNTHESIS AND PERSPECTIVES

This chapter links the outcomes of the PhD study (see chapters 3 – 5) to the current state of science, highlights key conclusions, and discusses limitations and research perspectives.

6.1 SYNTHESIS AND KEY FINDINGS

This thesis aimed to gain insight into what governs the levels and fate of small MPs in the Seine River under different hydrological conditions and in relation to urban MP sources (Figure 6–1). An additional goal was to compare different sampling methods. Therefore, MP monitoring on a larger spatiotemporal scale in the Seine River was conducted, and MP abundance was analyzed under various flow conditions and in relation to urban sewer discharges. A comprehensive monitoring dataset was composed as the basis for the analyses and for transparent data reporting, including the first quantification of field data and the collection and pre-processing of third-party data. In addition, two MP sampling devices were assessed in the field.

In **chapters 3 and 4 (papers I and II)**, the abundance of microplastic in the surface water in the Seine River upstream, in the urban center, and downstream Paris was studied. Specifically, MP concentrations were assessed and quantified as MP load along six locations spread over 420 km along the river every four months (July 2021, November 2021, February 2022, July 2022) for one year covering different river flow regimes. In addition, MPs were investigated in relation to inputs from urban sewer discharges in Paris to assess the potential contribution from this conurbation.

- MP field study covering temporal (flow regime) and spatial (urban) gradients
- Quantification of MP load in a mass balance
- Assessment of the impact of urban discharges on MP abundance

In **chapter 3**, MP monitoring data were pre-processed and compiled into a comprehensive dataset. The MP data from a total of 28 measurements (six sites × 4 campaigns from the Seine River, one site × 4 campaigns from the Marne River) were derived from field sampling using a novel sampling device and state-of-the-art sample and analytical processing. All samples were fully analyzed, and the reported data includes individual particle information, including dimensions and polymer types, MP concentrations and loads, and hydrometeorological parameters, such as river flow, precipitation, and suspended solids. Hydrological regimes were evaluated, a water balance for the Seine River was developed, and discharge volumes from WWTPs and CSOs were included. Results showed widespread MP pollution, with concentrations comparable to other studies, ranging from 14 to 4,700 particles m^{-3} and spatiotemporal variations moderately correlated to river flow. High precipitation in July 2021 caused high flow conditions, followed by lower flows in November due to a prolonged dry period. MP abundances were consistently lower upstream, and polypropylene (PP), polyethylene (PE), and polystyrene (PS) were the most abundant polymer types, in line with the literature. The provision of

transparent and detailed data, this study established a solid foundation for subsequent analyses on MP dynamics, contributions of urban sources, and methodological comparisons conducted in the following papers.

Chapter 4 (paper II) builds on the dataset from chapter 3 and analyzes the spatial and temporal variations of MPs along the urban gradient of Paris, the influence of hydrology, and urban discharges. Differences in MP abundance were explored between high, mid, and low flow conditions. Transport and fate (retention and release or mobilization) of MPs along sampling sites were determined using an MP mass balance/MP load approach. This was extended by analyzing WWTP effluent and CSO data. The MP concentrations were higher during high river flow conditions. The analysis yielded uncertain results when assessing sampling sites individually, and local and temporary factors, such as precipitation and site-specific emissions, might strongly influence MP levels. The limited number and the range of the data constrained statistical options. In line with the literature, smaller MPs [25-300 µm] were more abundant (median: 80 µm). Up to 13 polymer types were detected at a single site, with polymer diversity higher in urban and downstream areas, reflecting the elevated contribution of urban sources to MP pollution and raising concerns about toxicological risks for freshwater ecosystems. PP, PE, and PS were prevalent, while other polymers were less frequent, underscoring the need to account for rare types in study design and methodology. The mass balance and discharge analysis revealed two key points. Precipitation facilitated urban discharges and triggered CSO and higher WWTP effluent discharge, followed by elevated MP concentration and load in the river. Secondly, the MP mass balance showed an increase in load from upstream to urban sites but was unbalanced, indicating potential retention and accumulation in the urban area, followed by periodic downstream transport during high river flow periods. The results provide a foundation for developing source-pathway-receptor or fate models for riverine MPs under varying environmental conditions and emphasize the need for high-resolution spatiotemporal analyses to understand MP pollution in river catchments.

Together, **chapters 3 and 4** provide a coherent picture of MP dynamics in the Seine River and display comprehensive data generation, reporting, and interpretation. The studies show that urban discharges, hydrological variability, and other unexplored factors influence MP fate. Robust, transparent datasets are crucial for analyzing field observations in relation to MP release pathways and transport. This integrated approach establishes a quantitative reference for further fate modeling and management applications.

In **Chapter 5 (paper III)**, the performance and comparison of two methods to sample MP in river water, a pump with *in-situ* filtration and a sediment trap, were investigated under field conditions. High-frequency samples were collected in parallel at the same site, complemented by previous tests for a broader assessment. Both methods consistently captured MPs and showed similar concentration and size patterns, though variability among high-frequency samples was high. When normalized to suspended or settled sediment, sediment trap samples often showed higher MP numbers, but overall contained fewer particles, which can lead to overestimations. Differences in polymer variety were also observed, with pump samples capturing a wider range. The results highlight that sample size and number of observations affect the reliability of results, especially under low MP concentrations, suggesting that longer or more frequent sampling improves robustness. Expressing MP concentrations per unit of suspended solids offers another

metric that captures the particulate property and might improve understanding and interpretation across studies. The results also indicate a gap in understanding of what is being measured and how accurate the results are. This demonstrates the importance of methodological choices, the necessity of reporting details and uncertainties to improve comparability and interpretation across studies, and the need for more accurate method comparisons and calibrations.

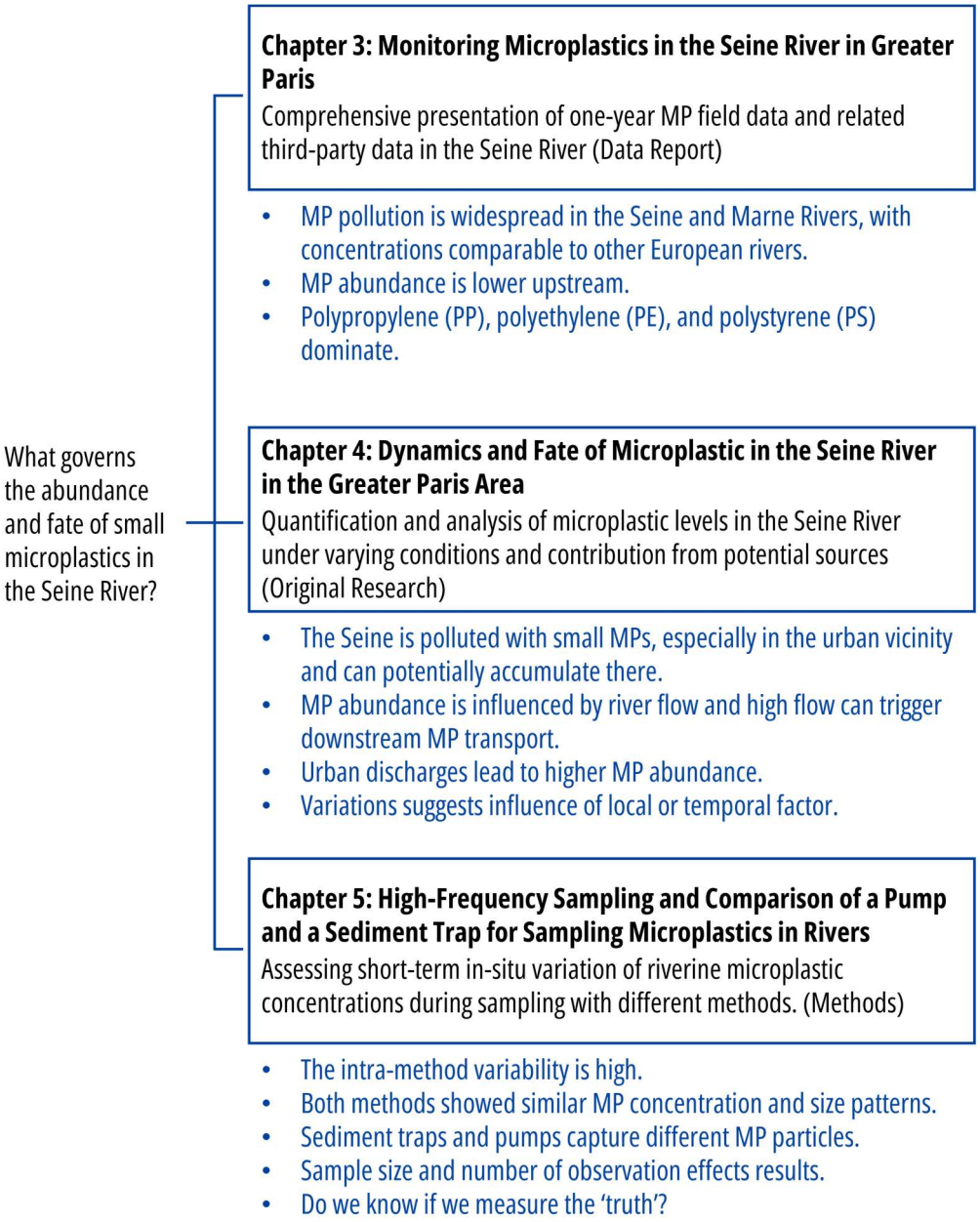

Figure 6–1 *Summary of the key findings of chapters 3, 4, and 5.*

6.2 LIMITATIONS

This PhD study provides new knowledge on microplastic (MP) pollution in an urban river. This knowledge can be used to improve understanding and further assessments on MP in the Seine River and draw new conclusions for MP monitoring and fate under environmental conditions.

Aspects such as the hydrometeorological conditions, site accessibility, and timing influenced the representativeness of samples. Different local parameters, like ship traffic, river morphology, and bank structure, possibly influenced MP fate but could not have be considered nor controlled in the sampling strategy. For example, shallow riverbanks may generate less turbulence and lower resuspension during high flow, while boat activity could increase MP redistribution. While a monitoring approach was followed, providing a more comprehensive study, the resolution of samples and the time (one year) were limited. This meant that the statistical power was limited. Sampling was conducted with a novel plastic-free pump, minimizing any field contamination. But the sampling was conducted from the riverbank, where conditions in a large river like the Seine were different than those in the middle of the cross sections, for example.

Analytical uncertainties are possible and can arise from sample processing and analysis, even though precautions to avoid sample contamination and work with high precision were taken. Despite following harmonized protocols, recovery efficiency and detection limits may have varied between samples or samples from the different methods, as sediment trap samples were size categorized in the lab instead of in the field as done with pump sampling, for example. Limited particle numbers in some samples might further introduce uncertainties and influence concentration estimates. General limitations of data availability and feasibility are smaller than the extent of analyses possible, for example, for the analysis of MP load and urban discharges. Interpreting MP fluxes and loads is complex and based on the assumption of homogeneous particle distribution, which we know is not true. Therefore, the interpretation of MP load is preliminary and can only be used as an estimate.

The studies in this thesis were designed to ensure high-quality MP data. Protocols were developed and followed for each procedure. Uncontrollable parameters such as weather and ecosystem conditions created challenging conditions and introduced uncertainty. Higher resolution and improvements in sampling strategy might have increased the usability of some data. This study provides a collection of MP data in an urban river and sheds new light on the fate of MP and methodological variability. Several studies approach the understanding of riverine MP under environmental conditions, and harmonization across studies could help acquire new knowledge and inform effective mitigation strategies.

6.3 CONCLUSIONS

The PhD study resulted in three scientific papers/manuscripts which together addressed the research topics:

- The abundance and fate of small MPs in Seine River in different flow conditions
- The impact of urban discharges on MP abundance in Paris
- The comparison of two methods to sample MPs in the upper water layer of a river

Research question 1: *What is the abundance of microplastics in the Seine River in the Greater Paris area under different river flow conditions* ***(papers I, II, and III)****?*

The studies showed that MPs are widespread throughout the Seine River catchment in Greater Paris, with concentrations up to 4,700 particles m^{-3}. MP concentrations and loads increased from upstream to urban and downstream sites and varied with river flow and hydrological events, such as extreme precipitation in July 2021. From the measured MPs [25 – 300 µm] smaller particles [<100 µm] were the most abundant, and polymer composition was dominated by PP, PE, and PS. The findings indicate spatiotemporal variability and that local and temporary factors strongly influence MP abundance and dynamics.

Research question 2: *What is the contribution of the Paris metropolitan area to the microplastic contamination in the Seine River* ***(papers I, II)****?*

The analysis of MP loads and urban discharge data revealed that wastewater treatment plant (WWTPs) effluent and combined sewer overflows (CSOs), contribute to MP contamination, particularly in urban and downstream sites. Polymer diversity was higher in urban areas, showing a possibly a larger variety of MP sources. Precipitation events increased MP release from the urban area, highlighting the role of both diffuse and point release pathways. This study provides novel insights into urban contributions to riverine MP pollution and demonstrates the importance of spatiotemporal variations, the need for high-resolution data, and comprehensive datasets.

Research question 3: *Is the method of microplastic sampling important to assess microplastics in the surface water of rivers* ***(paper III, IV, and V)****?*

A comparison of two sampling methods to capture riverine MPs, a pump with *in-situ* filtration and a sediment trap, showed that methodological choices strongly influence measured MP concentrations and types. With the pump, a higher number of MP particles and more types of polymers were captured in a shorter amount of time compared to the sediment trap. Both methods revealed comparable trends, but there was high variability per method and between methods. The novel approach of measuring MPs per suspended

sediment offers new opportunities to better understand the particulate fate of MPs. These results emphasize that sampling strategy, frequency, and replication critically affect data reliability and comparability. Methodological assessments must be conducted in future studies to support the standardization of MP sampling.

Overall, this thesis demonstrates that MP pollution in the Seine is spatially and temporally variable, influenced by urban discharges and hydrological conditions, and that sampling methodology influences what we observe. Together, the findings advance the understanding of MP abundance, release-pathways, and methodological considerations in urban rivers.

6.4 RESEARCH NEEDS AND OUTLOOK

This thesis gathered new knowledge and understanding of microplastic (MP) abundance and fate in the Seine River in Greater Paris and highlights new knowledge gaps that future research must address to advance in this field.

The first key point concerns the need for representative field data. The observed spatiotemporal variability in MP concentrations in the Seine suggests that sampling must be conducted at higher temporal and spatial resolution to accurately capture MP dynamics. More frequent and long-term monitoring is necessary to account for the large variability in urban river systems, including hydrological regimes, weather events, and site-specific activities, as these factors influence MP release, transport, and mobilization. Future studies should therefore prioritize robust strategies for acquiring high-quality datasets. Collaborative efforts, such as harmonizing methods, sharing protocols, and conducting simultaneous sampling, should be strengthened. High-quality, comparable data will bring research closer to accurately describing MP fate and support more reliable modeling approaches.

As outlined in paper III, the representativeness of field measurements is key for comparability. Future studies should aim to calibrate commonly used sampling methods under controlled conditions to better understand their accuracy and efficiency. While such validation is already standard for analytical techniques (e.g., FTIR), similar efforts are needed for sampling procedures. Moreover, data reporting should be harmonized to ensure future comparability and long-term data value. This thesis demonstrated that even within the same environment, different methods can yield different MP concentrations and polymer compositions. To address this, future research should emphasize methodological harmonization and detailed reporting of parameters such as sampling volume, duration, and environmental conditions. Standardized data summaries and reporting formats would enhance data comparability and reusability across studies.

This thesis also shows that MP concentrations are reported in a variety of units. A diversification and complementary use of units could improve comparability and environmental risk assessments. Reporting MPs in relation to suspended solids or as mass-based concentrations may provide more meaningful metrics for environmental evaluations. Another critical research need is the mapping of MP sources and release pathways in river environments. The higher polymer diversity seen in urban areas in this

study indicates multiple MP sources. To quantify their contributions, systematic assessments of urban discharges are required, supported by cross-sector collaboration. The results of this study provide a foundation for modeling MP fate in river environments but also emphasize the importance of including hydrological and meteorological factors. Climatic extremes, such as heavy rainfall or prolonged drought, should be explicitly considered in future research questions and monitoring strategies, as they increasingly influence MP pollution in urban systems.

Overall, this thesis demonstrates that, while considerable progress has been made in MP research, further advancement depends on methodological harmonization, accuracy, transparent reporting, and interdisciplinary collaboration. Future research faces the challenge of selecting appropriate methods for a complex group of pollutants while integrating existing, but often biased or limited data. The complexity of MP pollution in urban river systems presents both challenges and opportunities to generate knowledge that supports environmental management and policy development.

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APPENDIX

SUPPLEMENTARY MATERIAL FOR CHAPTER 3 148
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Supplementary Material for Chapter 3

Supplementary Information (SI)

Monitoring microplastics in the Seine River in the Greater Paris area.

Cleo N. Stratmann*, Rachid Dris*, Johnny Gasperi, Frans A. Buschman, Adriaan A. Markus, Sabrina Guerin, A. Dick Vethaak, Bruno Tassin

*** Correspondence:** Cleo N. Stratmann (Cleo.stratmann@enpc.fr), Rachid Dris (rachid.dris@u-pec.fr)

1 Universal Filtration Object (UFO)

This plastic-free, stainless-steel, and volume-reducing microplastic (MP) sampling pump was developed by Aalborg University (Denmark).

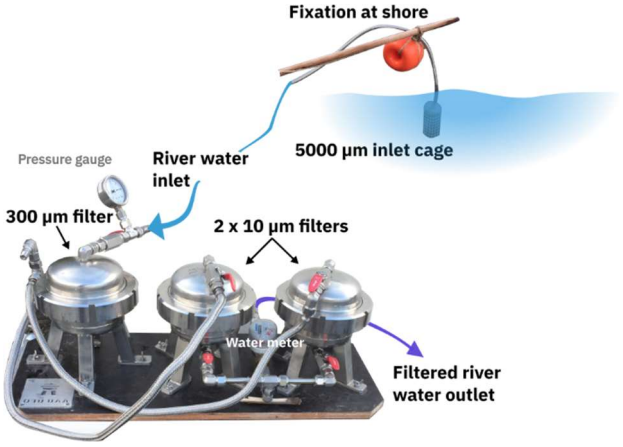


Figure S1 Set-up of the microplastic sampling with the UFO sampling pump.

2 µ-FTIR information

Type:	Nicolet iN10 (Thermofisher)
Obtained spectra:	Absorbance
Mode:	Transmission
Detector:	KBr imaging
Collection time:	1 scan
Spectral resolution:	8
No. of detectors:	16
Cell size:	25 x 25 µm
Spectral range:	4,000-400 cm^{-1}
Filter method:	Harris-Blackman
Correction:	Autobaseline
Background sample:	Yes, blank anodisc filter



Figure S2 FTIR machine Nicolet iN10

3 siMPle software information

Software version: 1.1.beta
Spectra library version: MP_Library_Extended_Grouped_1_5

4 Sample analysis process

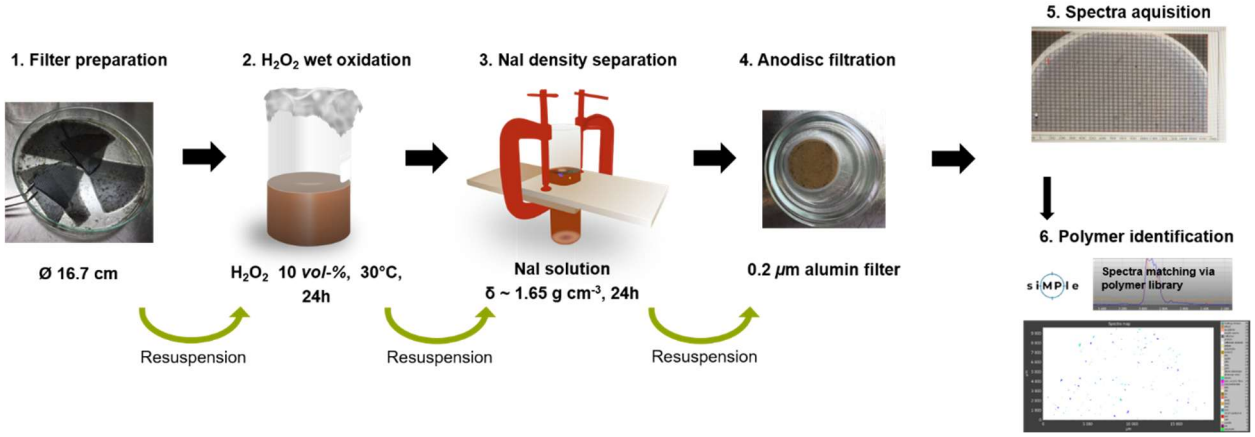


Figure S3 Visualization of the MP sample analysis process. H_2O_2=hydrogen peroxide, NaI=sodium-iodide, h=hours.

5 Polymer type distribution

Sixteen identified polymer types: Acrylonitrile butadiene styrene, acrylic, acrylic paint, alkyd, cellulose acetate, epoxy, polyamide, polyethylene (PE), polyester incl. polyethylene terephthalate, polypropylene (PP), polystyrene (PS), polyurethane, polyvinyl acetate, polyvinyl chloride, styrene-butadiene rubber, vinyl copolymer.

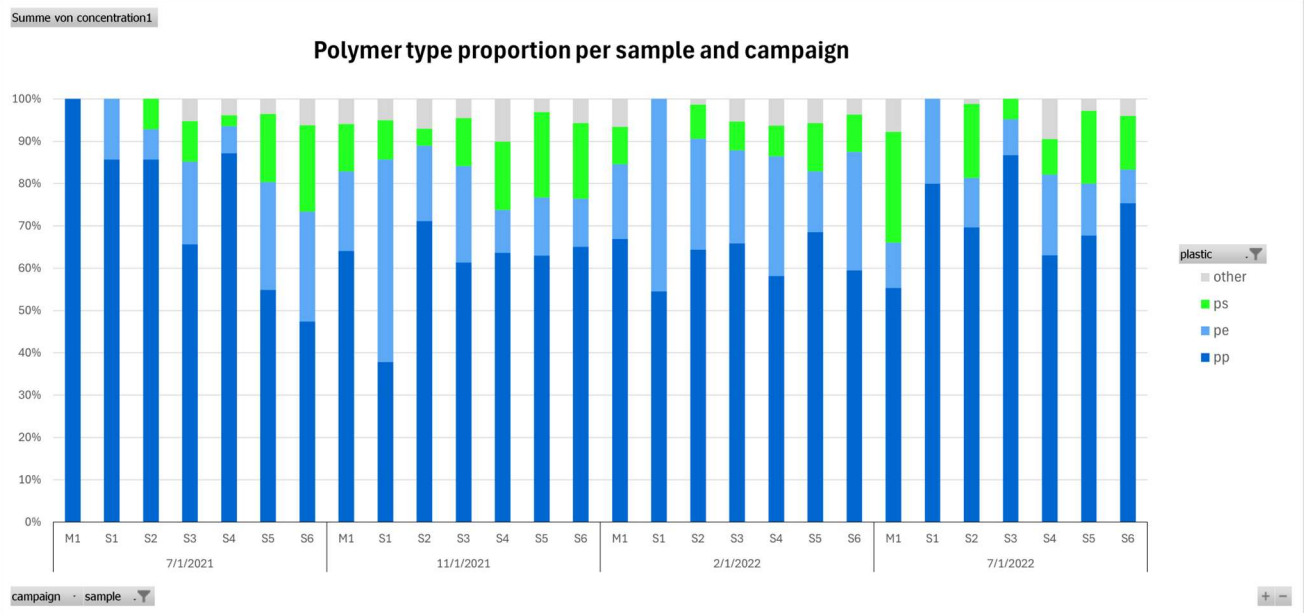


Figure S4 Polymer type proportions per sample and campaign with polypropylene (PP), polyethylene (PE), polystyrene (PS), and other polymer types aggregated (other). Campaigns named as 7/1/2021 for July 2021, 11/1/2021 for November 2021, 2/1/2022 for February 2022, and 7/1/2022 for July 2022.

6 Polymer size distribution

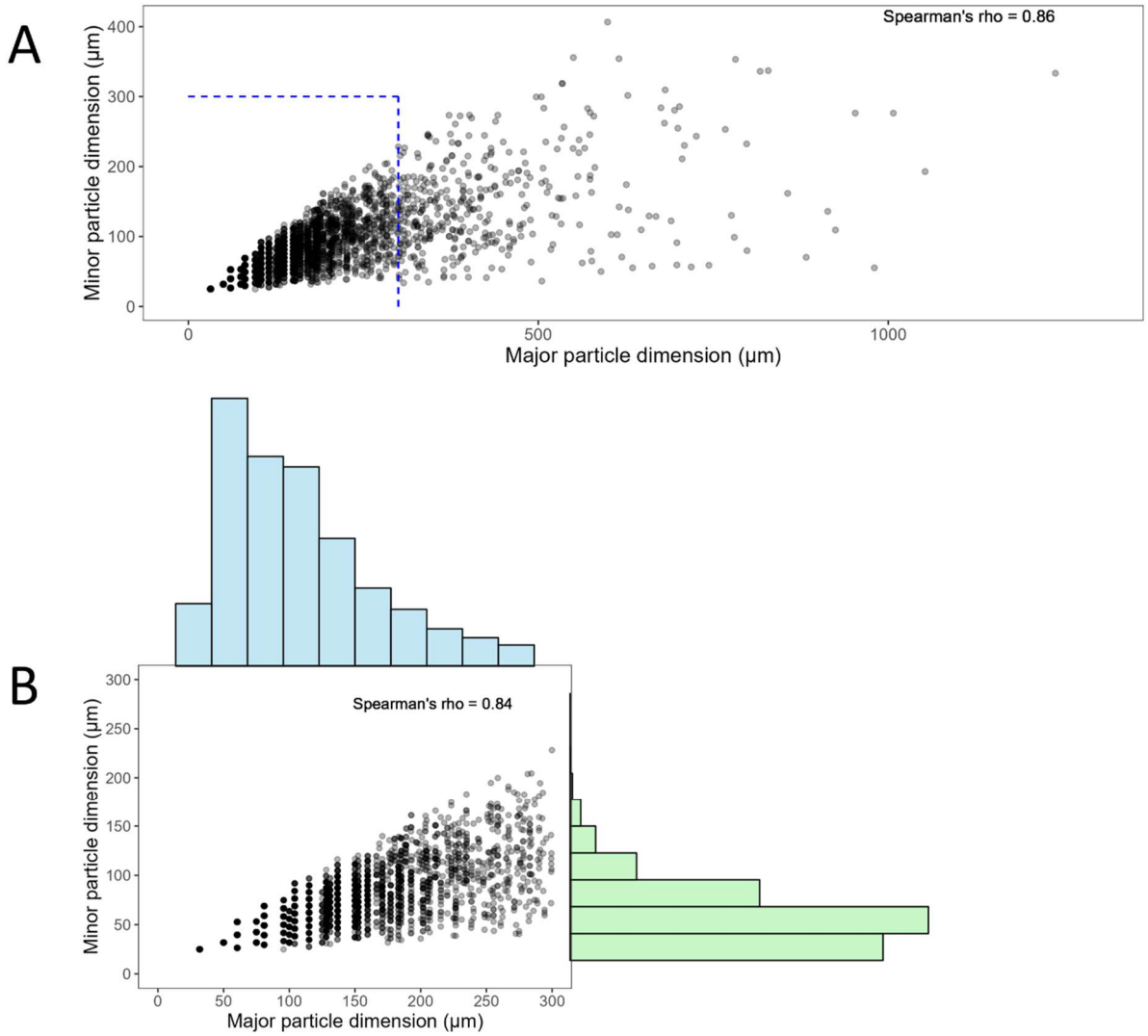


Figure S5 Minor and major microplastic particle dimensions and spearman rank correlation coefficient (rho) for all MP particles (A) and particles with major diameter <300 µm (B). Additional are histograms for minor and major particle dimension with a binwidth of 25 µm (B).

7 Seine River water balances

Five water balances were developed to assess the distribution and dynamics of the Seine River water within the monitoring area around Greater Paris over time. Negative deviations in the water balances (Figures S5-S10) suggest a deficit of water volumes downstream, and positive deviations indicate a potential additional inflow of water (precipitation, other discharge, other small tributaries). The following points should be considered to cause unaccounted differences in discharge: Hydraulic residence time between hydro stations, precipitation (e.g., hydrologic lag time), evaporation, discharge input from other smaller tributaries that were not included in the water balance, discharge from other sources (e.g., CSO, WWTP effluent), measurement inaccuracies, retention, and intake due to sluices or floodplains.

For each balance, the discharge at the relevant hydrostation of the Seine River is represented as the sum of the the discharge of the previous upstream hydrostation in the Seine River plus any additional instreaming tributaries (Table S1). Five water balances were developed for the hydrostations (Table S2) related to the MP sampling sites (S1-S6) between 1 June 2021, and 1 August 2022. The locations, details, and discharge data for the hydrostations are present in the dataset (*Metadata* and *Water-balance*).

- Water balance 1 (7.1): La Seine à Bazoches-les-Bray (F2400001)
- Water balance 2 (7.2): La Seine Seine-St Fargeau (F4470003)
- Water balance 3 (7.3): La Seine à Alfortville et à Villeneuve-Saint-Georges et à Vitry-sur-Seine (F490 0001)
- Water balance 4 (7.4): La Seine à Paris (Austerlitz) (F700 0001)
- Water balance 5 (7.5): La Seine à Vernon (H3200 001).

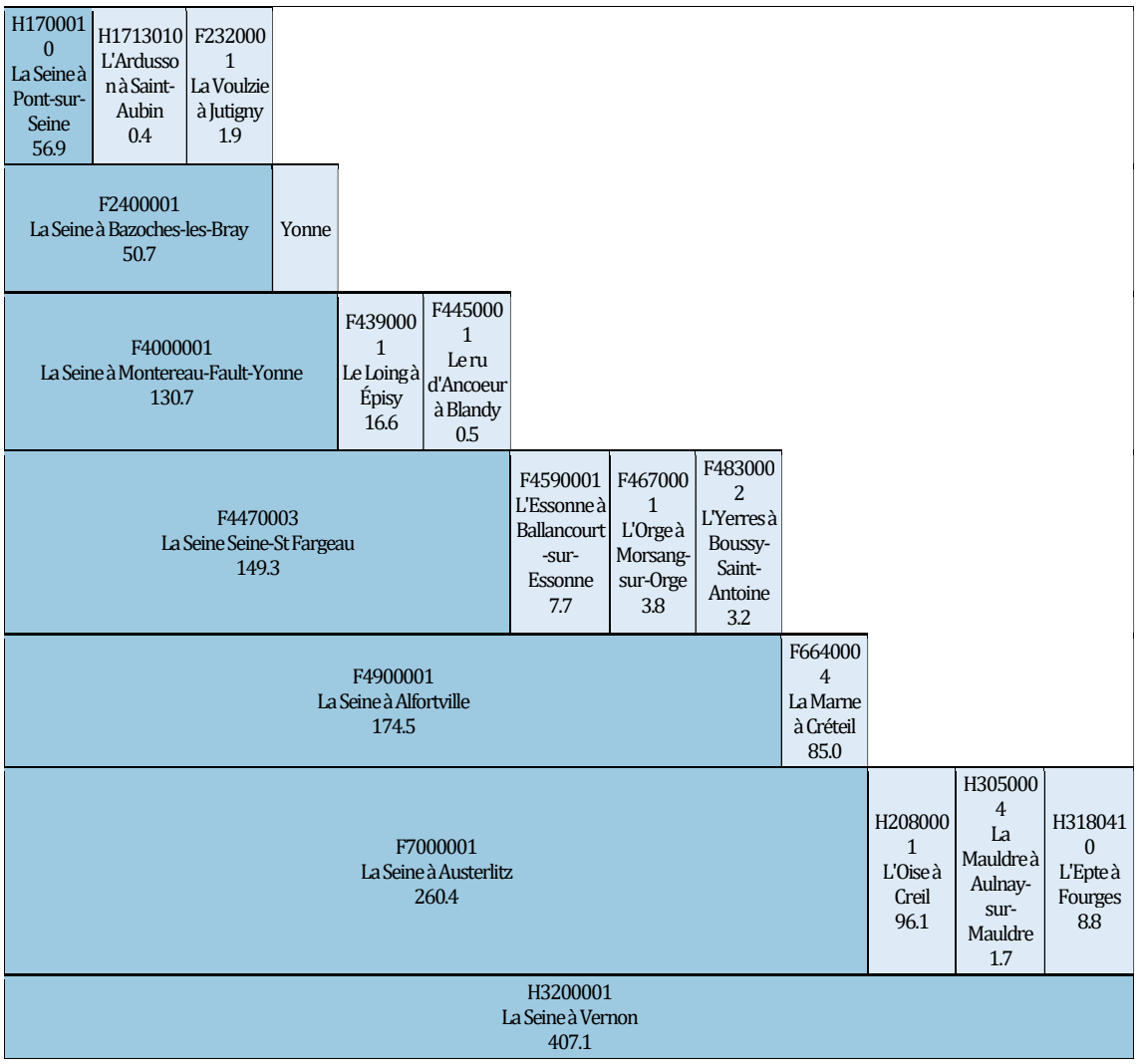
Discharge of the Yonne (Table 2) would be the difference between F4000001 (La Seine à Montereau-Fault-Yonne) and F2400001 (La Seine à Bazoches-les-Bray), however this part was omited here.

A water balance (7.6) was also developed for sampling site S5 (Triel-sur-Seine). The sampling site is located downstream of station F7000001 La Seine à Austerlitz and after the confluent of the Oise River (H2080001 L'Oise à Creil). To account for this addition of water, the discharges from both hydrostations are added to obtain the best estimate of river discharge at sampling site S5.

Table S1 Seine River and tributaries visualization for the water balances. This includes the hydrostation measurement points relevant for sampling sites S1 (La Seine à Pont-sur-Seine) until S6 (La Seine à Vernon). Flow direction reads from top to bottom across the horizontal field boundaries.

Seine	**Tributaries**											
La Seine à Pont-sur-Seine	Ardusson	Voulzie	Yonne	Loing	Ru d'Ancoeur	Essonne	Orge	Yerres	Marne	Oise	Mauldre	Epte
La Seine à Vernon												

Table S2 Water balance visualization. The table lists the hydrostation-IDs and the names of the hydrostations which daily river discharge data was obtained from. Light blue cells refer to tributaries (see also Table S1), and blue cells refer to the Seine. The balance includes the points of hydrostation measurements relevant for sampling sites S1 (La Seine à Pont-sur-Seine) until S6 (La Seine à Vernon). Flow direction reads from top to bottom across the horizontal field boundaries. The numbers represent mean discharge over the whole period as reported in the dataset (1 June 2021 – 1 August 2022) in m^3 s^{-1} for each hydrostation. Note that the Seine River discharge values relevant to the sampling sites (see dataset excel sheet *Data full* column W) differ up to 6-fold per site during MP samplings.



The following describes the hydrographs for the five different water balances. The absolute difference (orange lines) is calculated as the difference between the downstream discharge and the upstream discharge and any tributaries. The difference in river discharge would ideally be zero.

a. Water balance 1: F2400001 La Seine à Bazoches-les-Bray

$$Difference = Q_{F2400001} - Q_{H1700010} - Q_{F2320001} - Q_{H1713010}$$

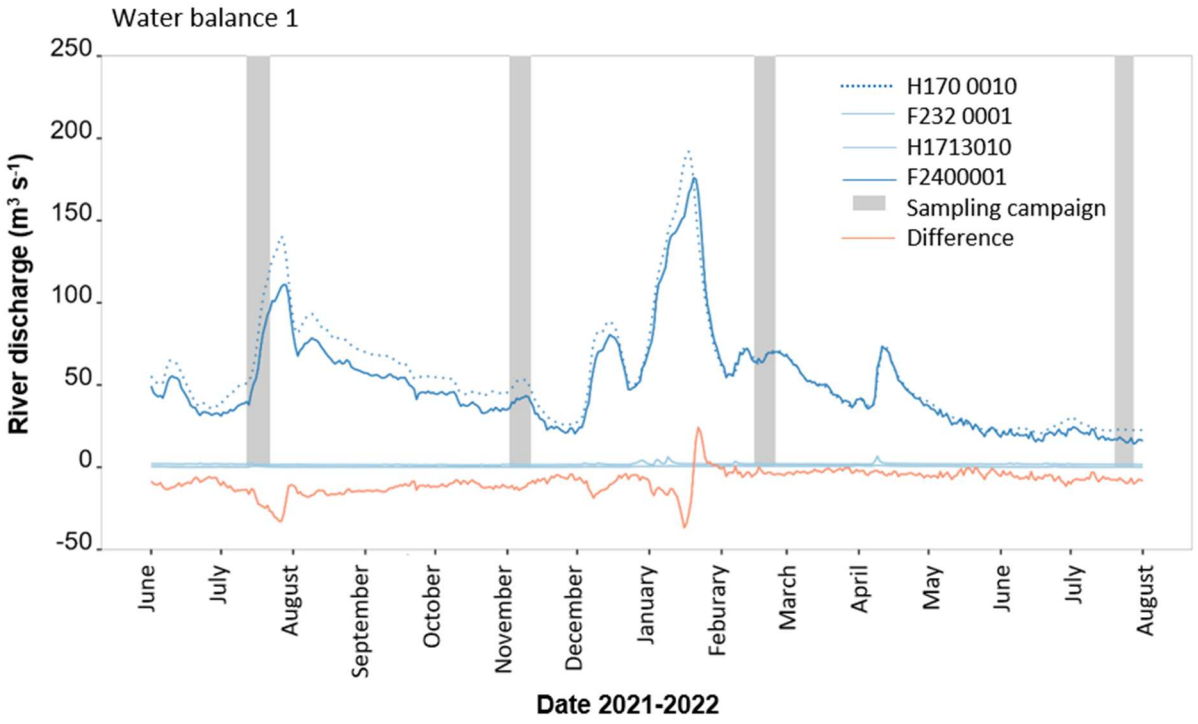


Figure S6 For sampling point S1, Marnay-sur-Seine, we consider the daily discharge from hydrostation H1700010, La Seine à Pont-sur-seine (dotted dark blue line). Tributaries La Voulzie (F2320001 – solid light blue line) and L'Ardusson (H1713010 – solid light blue line) are located downstream and discharges from both station are below ~10 m^3 s^{-1}. From station H1700010 until the next hydro station in the Seine river La Seine à Bazoches-les-Bray (F2400001 – solid dark blue line), the water balance results in discharge differences around zero, with values in the negative area, but with maximal deviances from zero of less than 50 m^3 s^{-1}.

b. Water balance 2: F4470003 La Seine Seine-St Fargeau

$$Difference = Q_{F4470003} - Q_{F4000001} - Q_{F4390001} - Q_{F4450001}$$

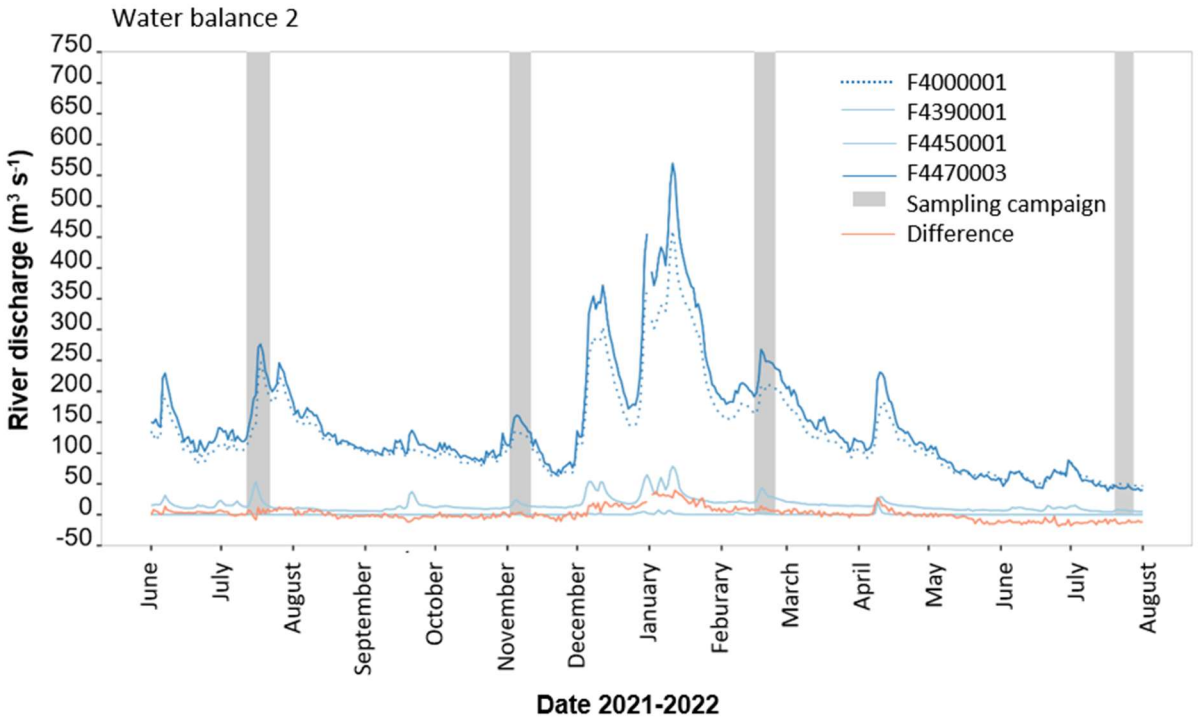


Figure S7 From station F4000001 La Seine à Montereau-Fault-Yonne until F4470003 La Seine Seine-St Fargeau the confluents Le ru d'Ancoeur à Blandy (F4390001) and Le Loing à Épisy (F4450001) join. Differences in discharge were slightly positive between December 2021 and February 2022 and more negative after May 2022.

c. Water balance 3 : F4900001 La Seine à Alfortville

$$Difference = Q_{F4900001} - Q_{F4470003} - Q_{F4590001} - Q_{F4670001} - Q_{F4830002}$$

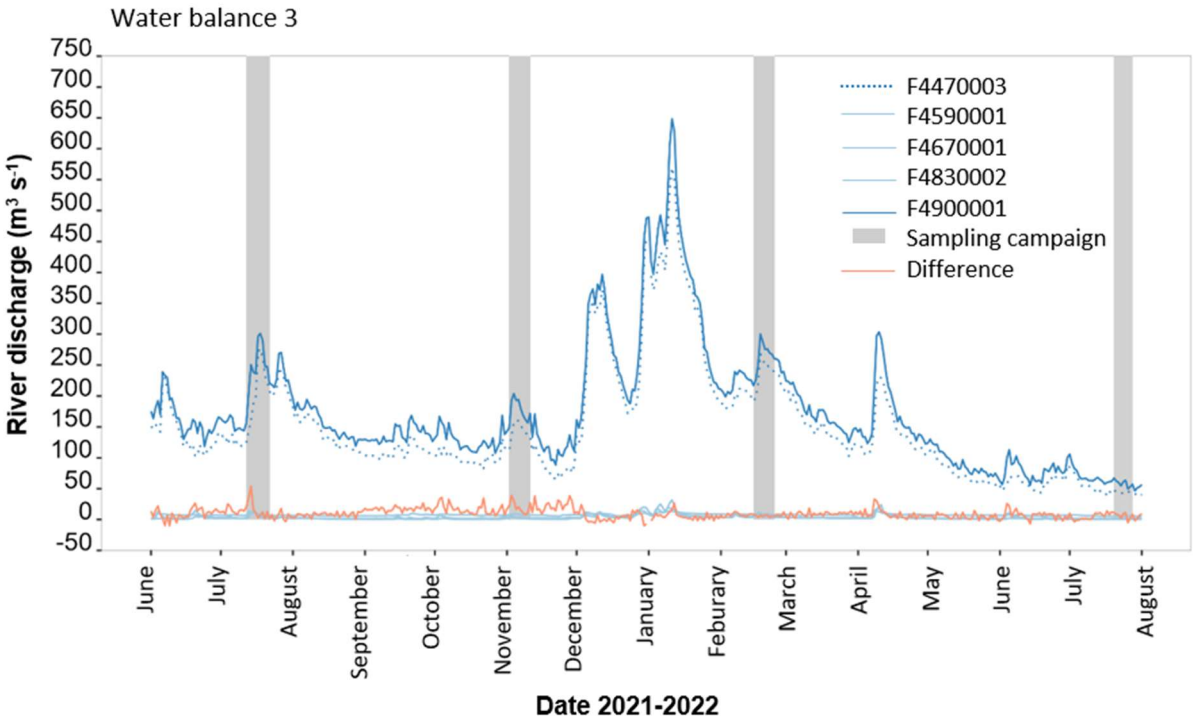


Figure S8 Between La Seine Seine-St Fargeau (F4470003) and La Seine à Alfortville (F4900001), the three confluents Essonne (F4590001), Orge (F4670001), and Yerres (F4830002) join. The balance exhibits only slight deviations.

d. Water balance 4: F7000001 La Seine à Paris (Austerlitz)

$$Difference = Q_{F7000001} - Q_{F4900001} - Q_{F6640004}$$

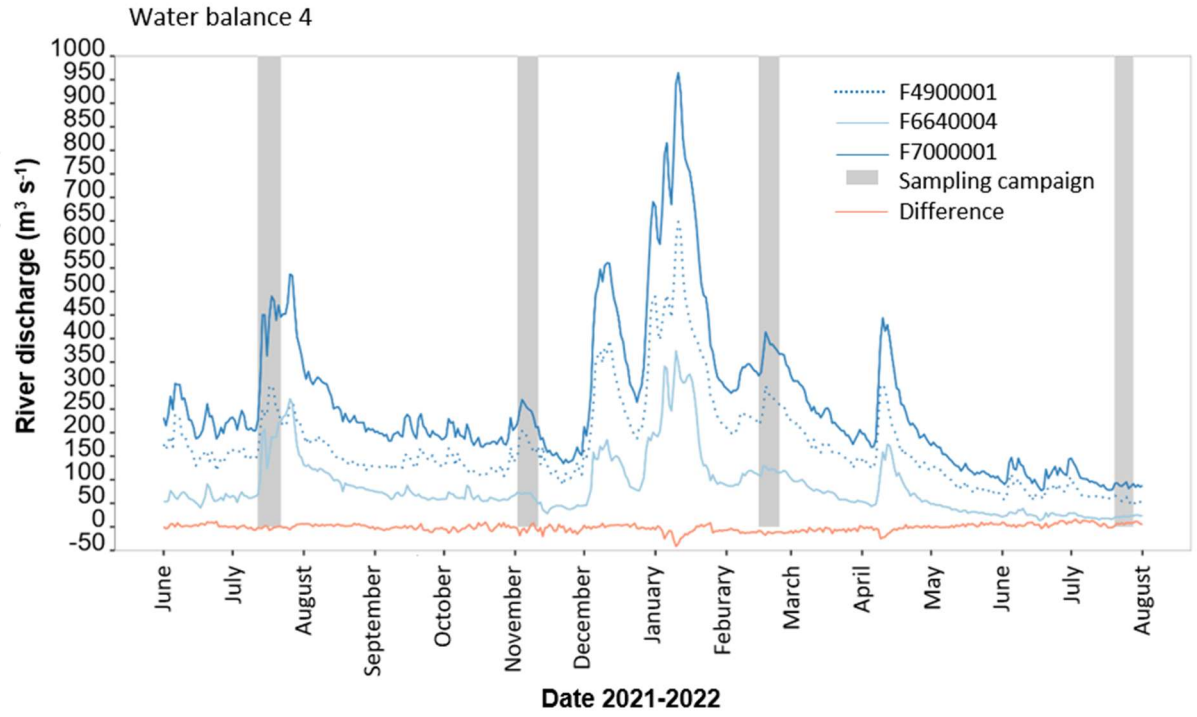


Figure S9 The water balance for station La Seine à Paris (F7000001) results from station La Seine à Alfortville (F4900001) and the confluent of the Marne (F6640004). Deviations are small.

e. Water balance 5: H3200001 La Seine à Vernon

$$Difference = Q_{H3200001} - Q_{F7000001} - Q_{H2080001} - Q_{H3050004} - Q_{H3180410}$$

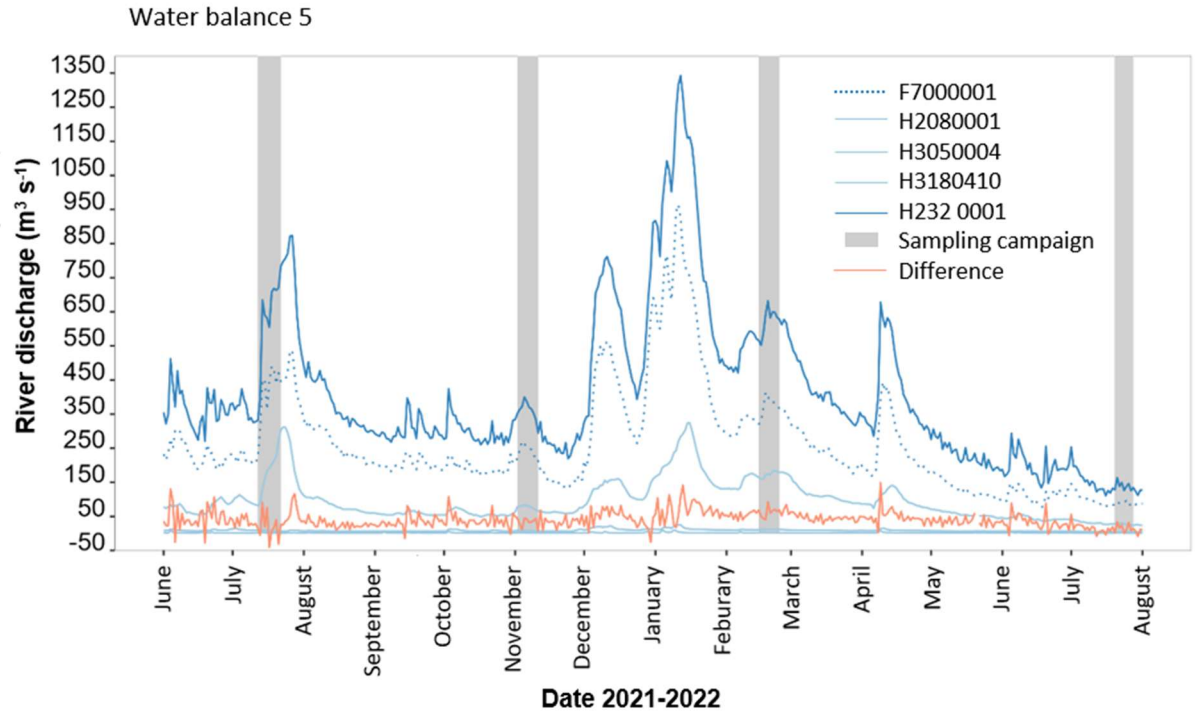


Figure S10 At station H3200001 (La Seine à Vernon), the discharge results from La Seine à Paris (F7000001) and three tributaries: Oise (H2080001), Mauldre (H3050004) and Epte (H3180410). Deviations are more often positive.

f. Water balance for sampling site S5 La Seine à Triel-sur-Seine

The sampling site S5 (Triel-sur-Seine) is downstream of hydrostations La Seine à Paris (F7000001) and the Oise confluent (H2080001). Therefore, the discharges from both hydrostations were added and are included in the dataset (Excel table sheet *data full*) as column named "River discharge (Q) of the Seine for S5 (m^3s^{-1})". No graphic is intended.

$$Q_{\text{Addition for S5}} = Q_{F7000001} + Q_{H2080001}$$

Supplementary Material for Chapter 4

Table SI 1 *Water quality parameter measurements per sampling*

Sample	Sampling campaign	Sampling sate (dd/mm/YYYY)	SSC (mg L-1)	Turbidity (NTU)	pH	Conductivity (µS cm-1)	Temperature (°C)	Flow velocity (m s-1)
S1		13/07/2021	29.16	5.13	7.9	429	17.8	0.25
S2		21/07/2021	30.72	6.22	7.9	432	21.0	0.01
M1		12/07/2021	25.88	6.27	7.9	577	19.6	NA
S3	Jul-2021	22/07/2021	51.67	23.43	7.8	439	21.0	NA
S4		16/07/2021	22.74	13.63	7.7	486	19.9	0.03
S5		20/07/2021	48.29	20.53	7.5	470	21.0	0.04
S6		19/07/2021	17.74	8.53	7.7	536	22.2	0.05
S1		03/11/2021	0.54	2.86	7.7	372	11.6	0.34
S2		09/11/2021	3.88	5.61	7.8	456	10.5	0.01
M1		02/11/2021	21.68	8.11	7.8	479	11.8	0.01
S3	Nov-2021	11/11/2021	4.40	4.64	7.8	486	10.1	NA
S4		10/11/2021	17.19	6.82	7.7	513	10.9	0.37
S5		11/11/2021	6.93	7.09	7.7	590	10.5	NA
S6		04/11/2021	5.28	4.84	7.5	580	12.1	0.03
S1		22/02/2022	19.02	16.40	8.2	516	9.0	0.34
S2		17/02/2022	11.09	9.13	8.2	631	8.5	NA
M1		15/02/2022	14.6	14.17	8.2	580	7.3	0.03
S3	Feb-2022	16/02/2022	11.39	13.03	8.2	538	8.7	NA
S4		21/02/2022	32.93	18.80	8.2	550	9.1	0.06
S5		23/02/2022	23.02	23.67	8.0	571	9.4	NA
S6		24/02/2022	24.88	20.60	8.0	571	9.1	0.07
S1		22/07/2022	1.68	3.19	7.9	407	22.1	0.15
S2		21/07/2022	2.54	2.67	7.6	475	25.6	-0.02
M1		27/07/2022	2.54	2.69	7.7	605	24.3	0
S3	Jul-2022	20/07/2022	2.71	2.64	7.5	555	25.9	NA
S4		28/07/2022	8.38	4.21	7.5	572	24.4	-0.01
S5		26/07/2022	11.64	14.00	7.8	661	24.1	-0.05
S6		25/07/2022	3.53	3.14	7.4	720	25.6	-0.02

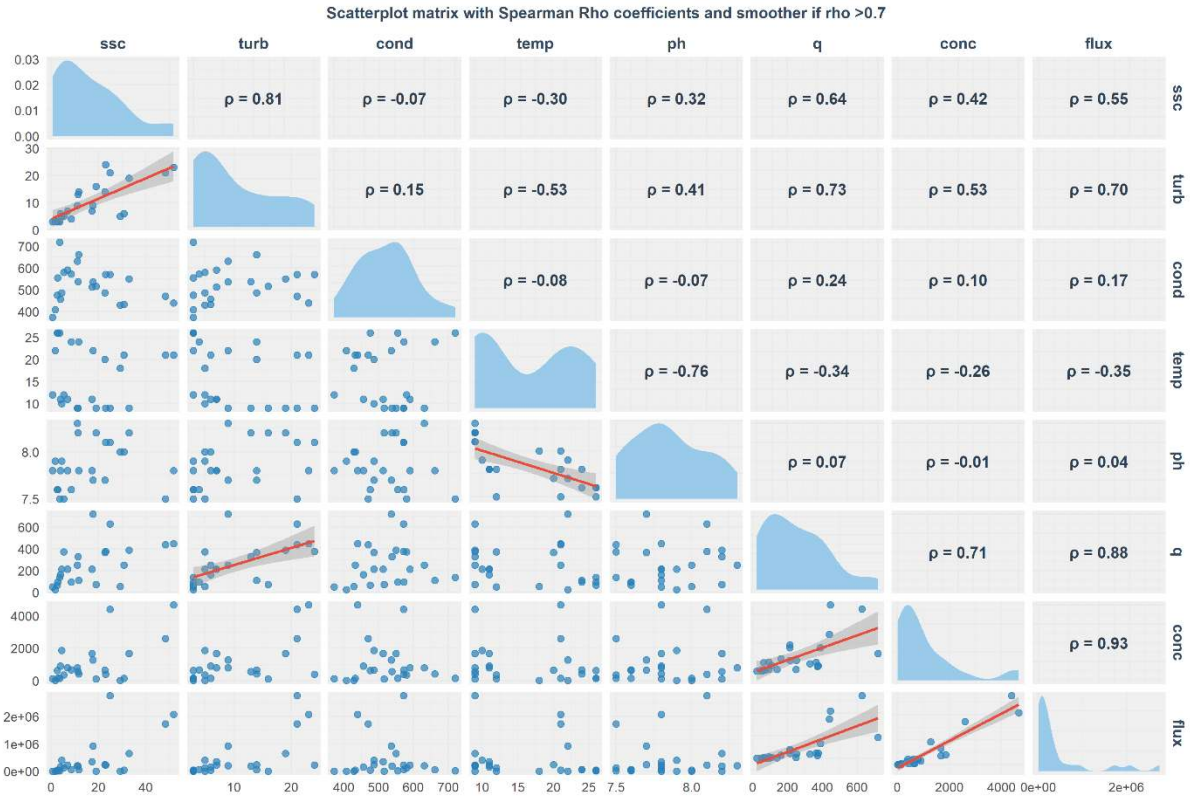


Figure SI 1 *This scatterplot displays the different relationships between environmental, hydrological and pollutant parameters: SSC (ssc in mg L-1), turbidity (turb in NTU), conductivity (cond in µS cm-3), temperature (temp), pH (ph), river discharge (q in m3 s-1), MP flux (fluxs in particles s-1), MP concentration (conc in particles m-3). Data points are from Seine River samples (N=24). Blue graphs in the middle section display the data distribution of each parameter.*

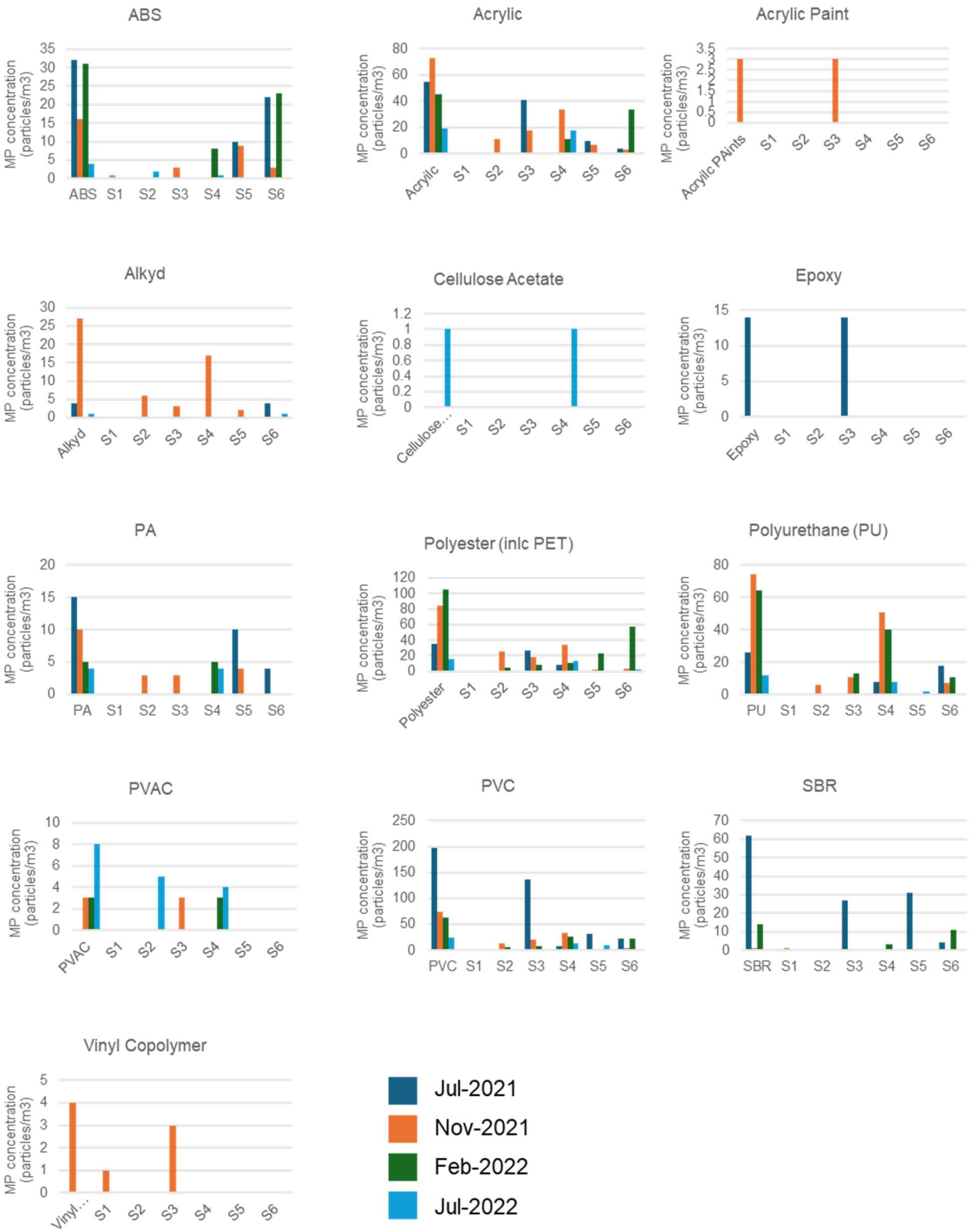


Figure SI 2 *MP concentrations by sample separately for each polymer type (other than PE, PP, PS). First section on x-axis represents the summary of concentrations by campaign, y-axes scales vary.*

Table SI 2 *Kruskal-Wallis rank sum test results for polymer type detection frequency types across different sampling sites (S1, S2, S3, S4, S5, and S6).*

Kruskal-Wallis rank sum test for all sampling sites in the Seine excluding data points from the Nov-2021 campaign, N=18:
data: x and group, N=18
Kruskal-Wallis chi-squared = 12.6775, df = 5, p-value = 0.03

Comparison of x by group
(No adjustment)

Col Mean-| Row Mean	S1	S2	S3	S4	S5
S2	-1.115773				
	0.1323				
S3	-1.731371	-0.615598			
	0.0417	0.2691			
S4	-3.039519	-1.923746	-1.308147		
	0.0012*	0.0272	0.0954		
S5	-1.654422	-0.538649	0.076949	1.385097	
	0.0490	0.2951	0.4693	0.0830	
S6	-2.847145	-1.731371	-1.115773	0.192374	-1.192722
	0.0022*	0.0417	0.1323	0.4237	0.1165

alpha = 0.05
Reject Ho if p <= alpha/2

Kruskal-Wallis rank sum test for all sampling sites in the Seine, N=24:

kruskal.test(variety ~ site, data = polymer_variety)
data: variety by site N=24
Kruskal-Wallis chi-squared = 7.5981, df = 5, p-value = 0.1798
dunn.test(polymer_variety$variety, polymer_variety$site, kw = TRUE, label = TRUE)

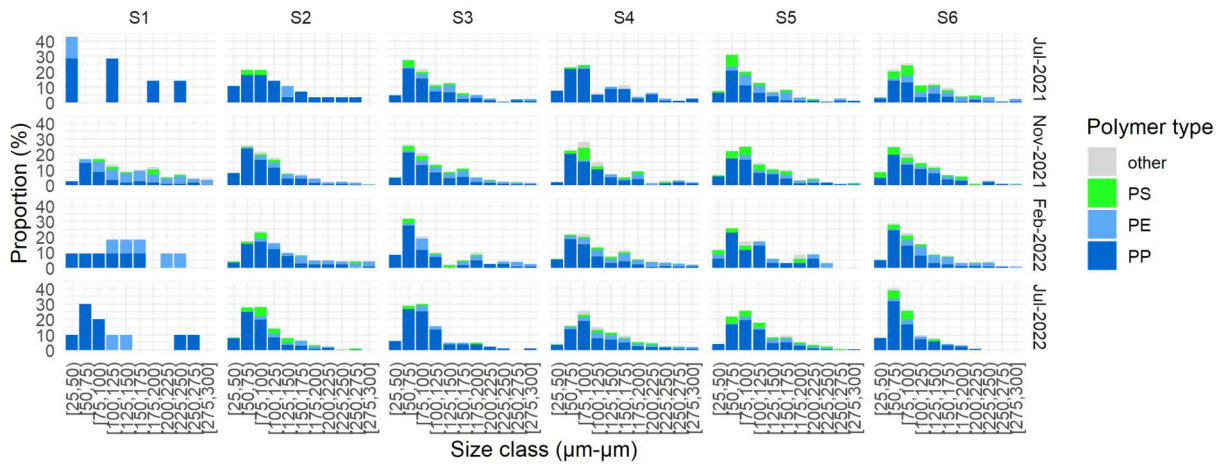


Figure SI 3 *Proportions of polymer types per sampling site (horizontal panels) shown across 25 µm-size bins. Proportions were calculated from MP number concentrations. The sum of proportions per sample (panel) adds up to 100%. Vertical panels represent sampling campaigns.*

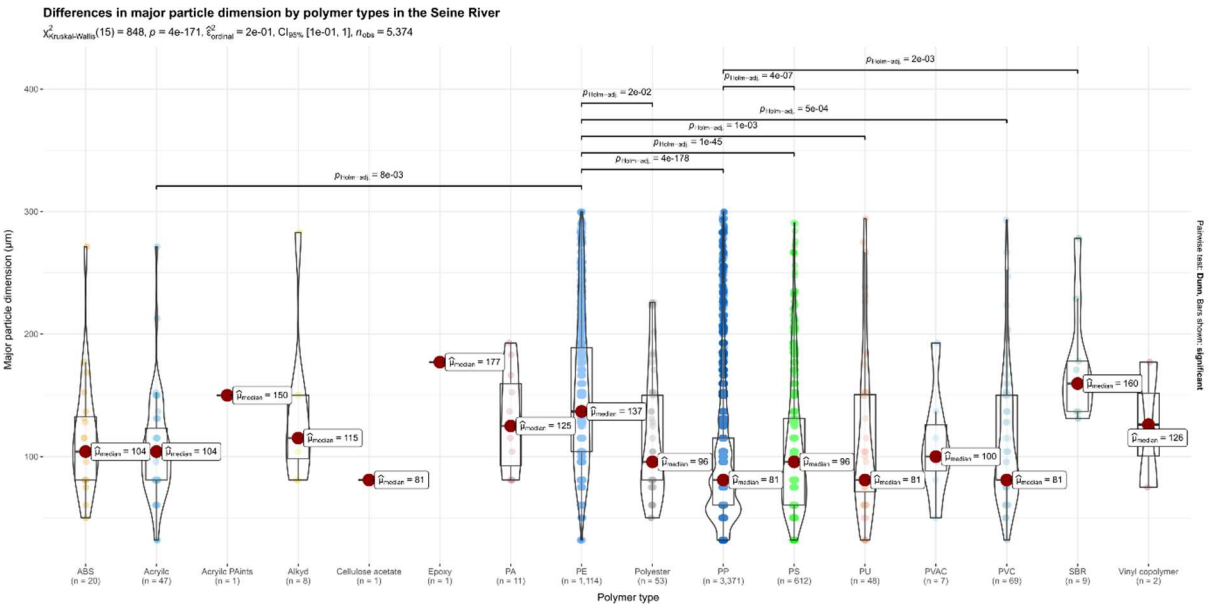


Figure SI 4 *Violin plots show the distribution of MP major particle dimension across polymer types for all particles of Seine samples (S1-S6, N=5384). For the interpretation of a violin plot including probability density function (PDF) as used here, we recommend visiting this website: https://www.labxchange.org/library/items/lb:LabXchange:46f64d7a:html:1*

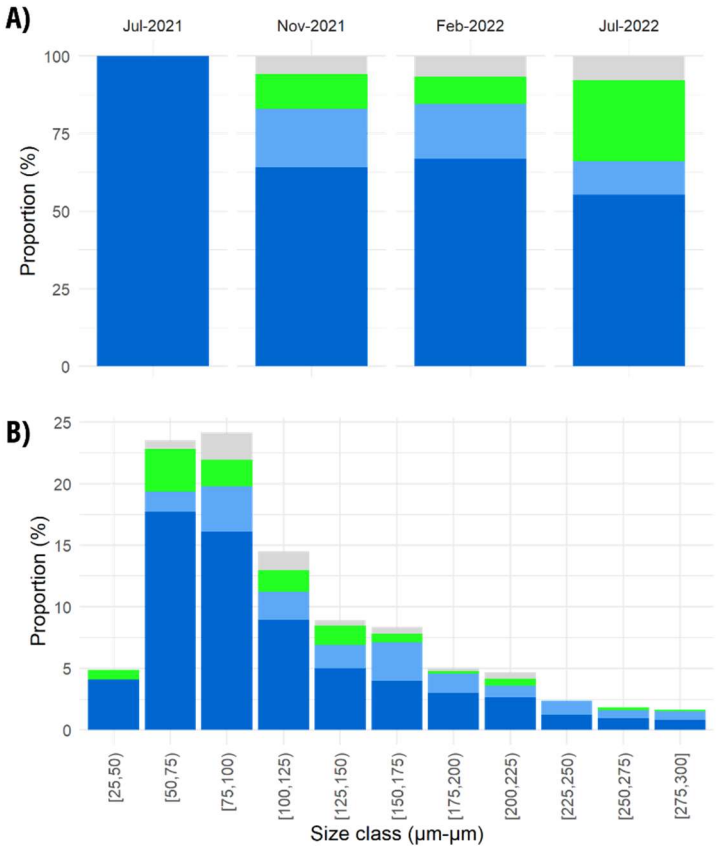


Figure SI 5 *Polymer type proportions for sampling sites in the Marne River (M1) (A) across campaigns and (B) across size bins.*

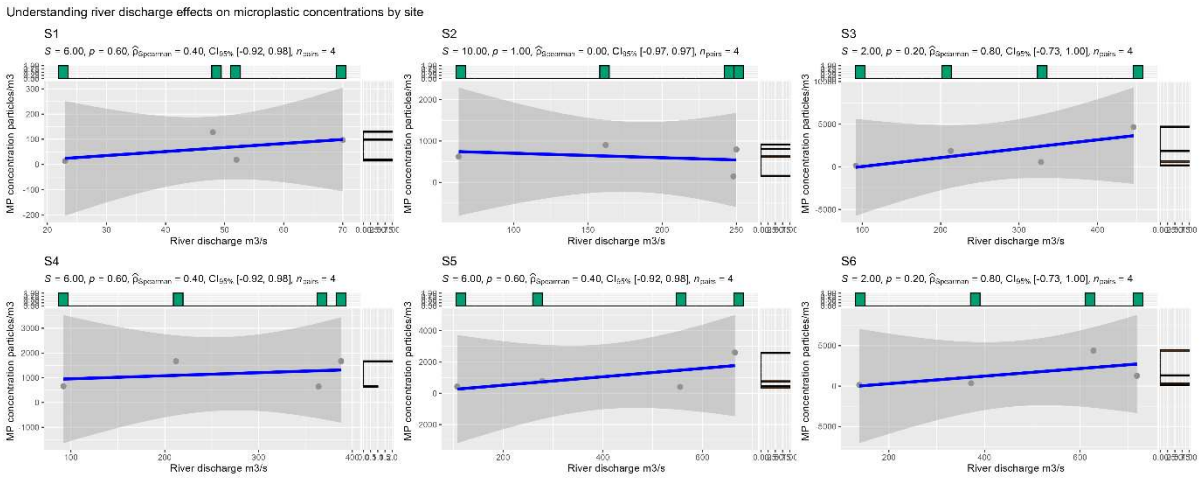
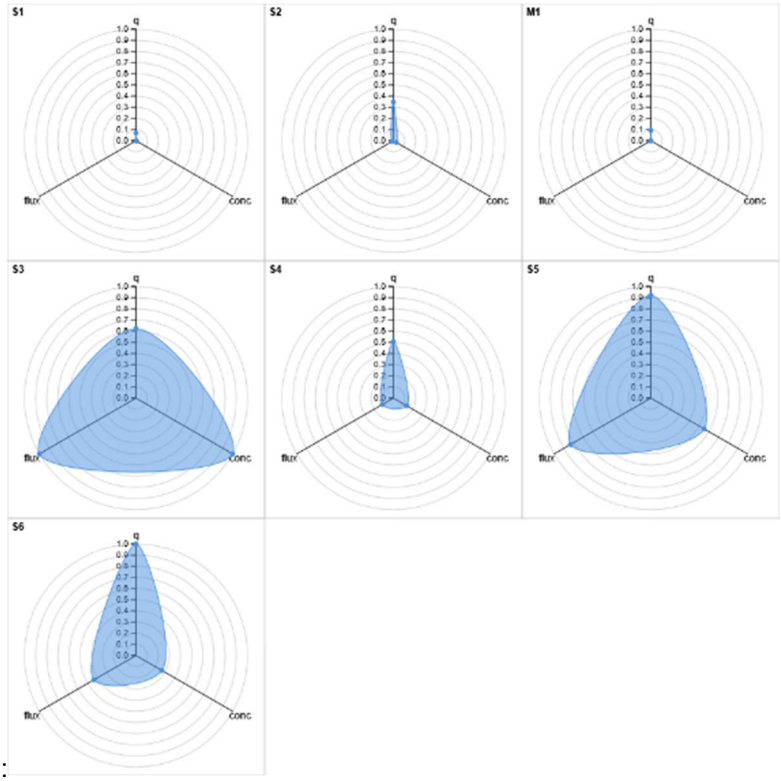
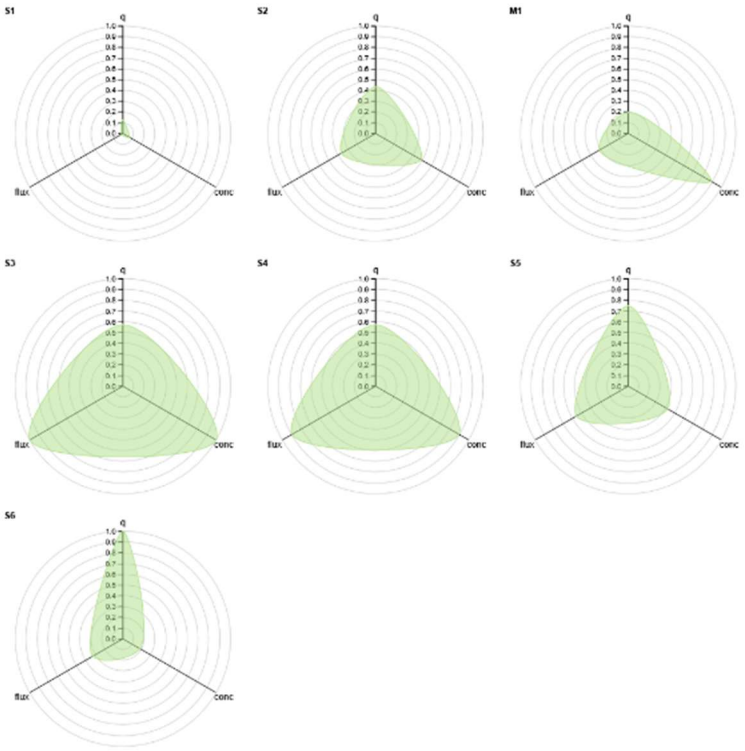


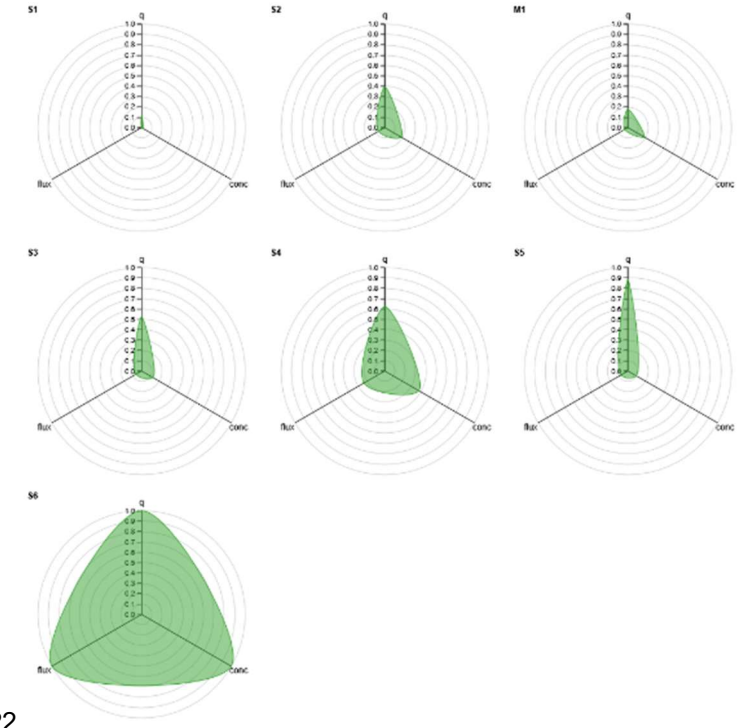
Figure SI 6 *River discharge (x-axis) against MP concentration (y-axis) by sampling site for all samples in the Seine River (S1-S6, N=24). Aware the different scales on x and y-axes. Secondary axes and graphs display data distribution.*



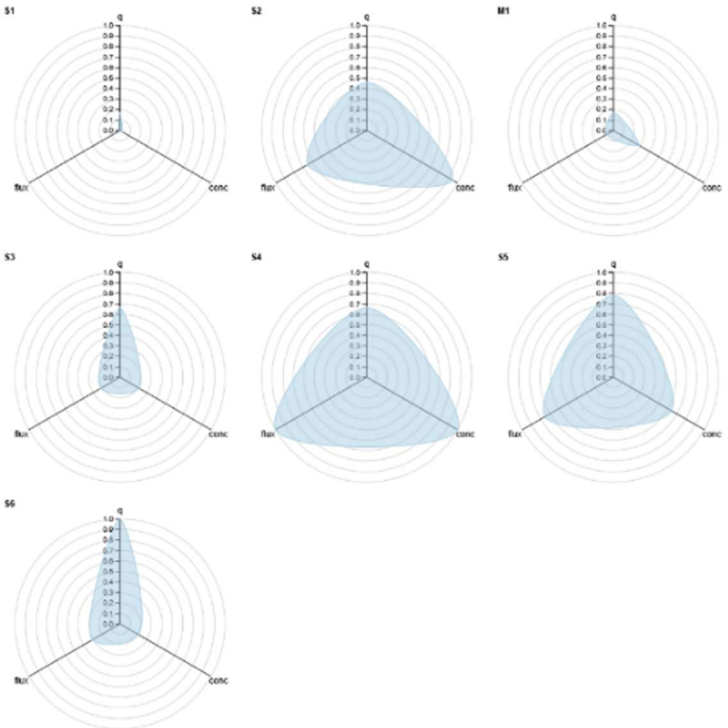
Jul-21:



Nov-21:



Feb-22



Jul-22

Figure SI 7 *(A) Radar plot from the July 2021 (B) Radar plot from the November 2021 campaign.(C) Radar plot from the February 2022 campaign. Normalized by maximum values per variable of the campaign. (D) Radar plot from the July 2022 campaign. Normalized by maximum values per variable of the campaign.*

Table SI 3 *Basis for the display of radar plots (Figures 12); Parameters were normalized per maximum value of each campaign.*

site	campaign	q	conc	flux	Flux_mass
S1		0.072	0.004	0.000	0.000
S2		0.345	0.031	0.017	0.018
M1		0.095	0.003	0.001	0.000
S3	July 2021	0.620	1.000	1.000	1.000
S4		0.506	0.138	0.112	0.113
S5		0.925	0.557	0.830	0.628
S6		1.000	0.273	0.440	0.478
S1		0.129	0.069	0.016	0.025
S2		0.435	0.486	0.369	0.278
M1		0.199	0.888	0.309	0.264
S3	November 2021	0.573	1.000	1.000	0.973
S4		0.570	0.897	0.893	1.000
S5		0.747	0.426	0.556	0.459
S6		1.000	0.187	0.327	0.245
S1		0.111	0.022	0.002	0.004
S2		0.398	0.182	0.072	0.116
M1		0.175	0.182	0.032	0.042
S3	February 2022	0.522	0.127	0.066	0.084
S4		0.618	0.381	0.235	0.316
S5		0.884	0.092	0.081	0.054
S6		1.000	1.000	1.000	1.000
S1		0.167	0.022	0.005	0.004
S2		0.457	0.944	0.646	0.362
M1		0.167	0.284	0.071	0.100
S3	July 2022	0.667	0.215	0.215	0.130
S4		0.667	1.000	1.000	1.000
S5		0.783	0.644	0.756	0.616
S6		1.000	0.203	0.305	0.124

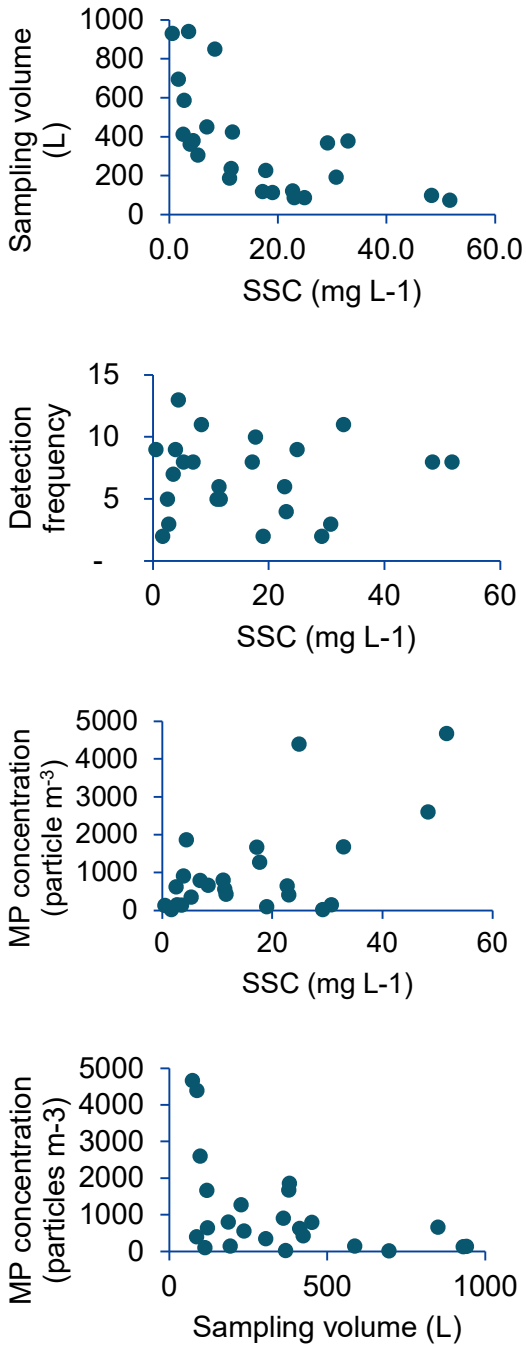


Figure SI 8 (*A) Relationship between SSC concentration and sampling volume for sampling sites in the Seine River (S1-S6, N=24). There is a clear power-law relation suggesting that with higher SSC we obtained lower sampling volume, highlighting the role of suspended solids to the filter clogging during sampling with a 300µm and 10µm filter-cascade setup. (B) The relationship between SSC concentration and detection frequency of different polymer types in a sample. There is no noticeable trend, suggesting that SSC is not relevant for the number of different polymers found. (C) The positive relations between SSC and MP concentration per sample is noticeable. (D) MP concentration and sampling volume showing high MP concentrations were obtained despite lower sampling volumes.*

Supplementary Material for Chapter 5

Supplementary Information (SI)

Sampling site



Figure SI 1 A plastic gyre observed 360 m downstream from the Bougival sampling site. The photo was taken from the bridge 'Pont Abbe Pierre' at the site of Île de loge in July 2022. The river flow direction is from left to right.

Sampling duration

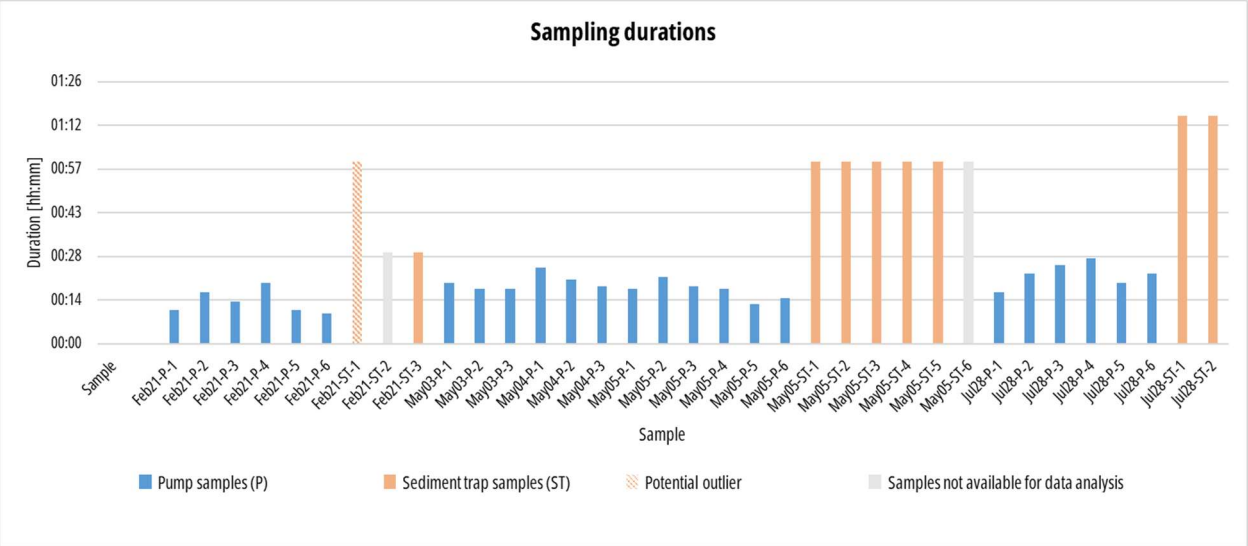


Figure SI 2 Sampling duration of all samples.

Table SI 1 Sampling start and end times and duration. Times according to CET for Feb21-samples, otherwise CEST.

Sample	Start time (hh:mm)	End time (hh:mm)	Duration (hh:mm)
Feb21-P-1	12:55	13:06	00:11
Feb21-P-2	13:15	13:32	00:17
Feb21-P-3	13:36	13:50	00:14
Feb21-P-4	13:55	14:15	00:20
Feb21-P-5	14:30	14:41	00:11
Feb21-P-6	14:50	15:00	00:10
Feb21-ST-1	14:30	15:30	01:00
Feb21-ST-2	15:30	16:00	00:30
Feb21-ST-3	16:00	16:30	00:30
May03-P-1	12:40	13:00	00:20
May03-P-2	13:07	13:25	00:18
May03-P-3	13:38	13:56	00:18
May04-P-1	12:55	13:20	00:25
May04-P-2	13:26	13:47	00:21
May04-P-3	13:56	14:15	00:19
May05-P-1	10:22	10:40	00:18
May05-P-2	11:35	11:57	00:22
May05-P-3	12:35	12:54	00:19
May05-P-4	13:35	13:53	00:18
May05-P-5	14:35	14:48	00:13
May05-P-6	15:35	15:50	00:15
May05-ST-1	10:00	11:00	01:00

May05-ST-2	11:00	12:00	01:00
May05-ST-3	12:00	13:00	01:00
May05-ST-4	13:00	14:00	01:00
May05-ST-5	14:00	15:00	01:00
May05-ST-6	15:00	16:00	01:00
Jul28-P-1	11:55	12:12	00:17
Jul28-P-2	12:23	12:46	00:23
Jul28-P-3	12:54	13:20	00:26
Jul28-P-4	13:25	13:53	00:28
Jul28-P-5	13:59	14:19	00:20
Jul28-P-6	14:25	14:48	00:23
Jul28-ST-1	12:30	13:45	01:15
Jul28-ST-2	13:45	15:00	01:15

ST sampling device

Table SI 2 ST technical details taken from Bionef® and HydroBios®.

Technical details	
Height	1200 mm
Diameter	320 mm
Opening area	0.015 m^2
Cylinder diameter (own calculation)	~138 mm
Grid dimensions	20 x 20 x 40 mm
Weight	12 kg
Frame material	Titanium
Cylinder material	PVC
Other materials	PTFE

ST sample treatment

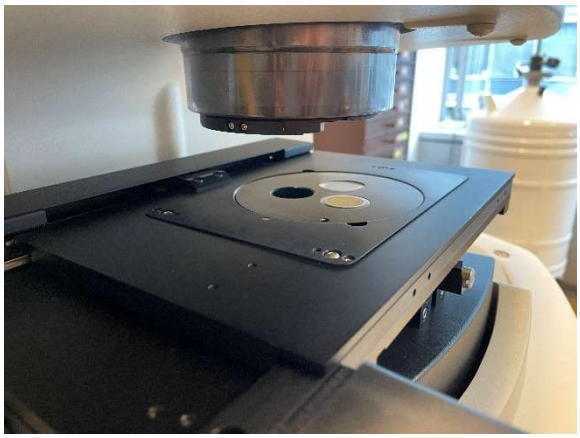
The whole ST sample was poured on a 10 µm stainless-steel filter using a clean glass-filtration set-up. The sample bottle and the filtration funnel were rinsed trice. The filtrate was then poured from the ground joint flask onto a 0.7 µm GF/F filter to capture SSC.

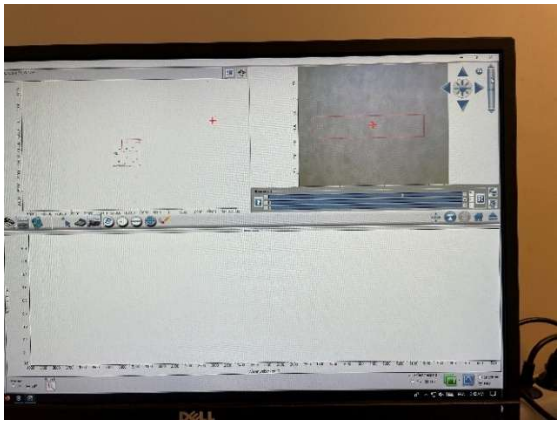
The steel and GF/F filter, both were placed in the dry oven (60C) for >48 hours, then one hour in the desiccator. Filters were weighed for the DW.

FTIR analysis



Figure SI 3 FTIR filter set up with sample and blank filter





FTIR blank calibration

Results – physico-chemical parameters

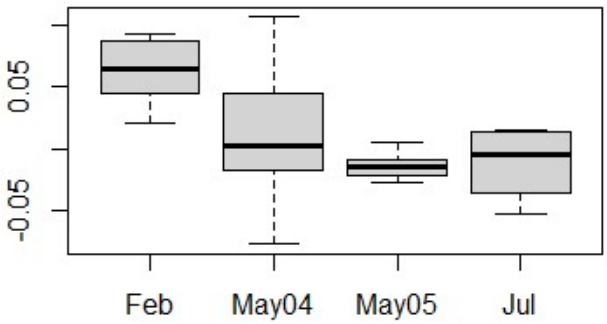


Figure SI 4 Flow velocity measurements at sampling location across the five sampling days

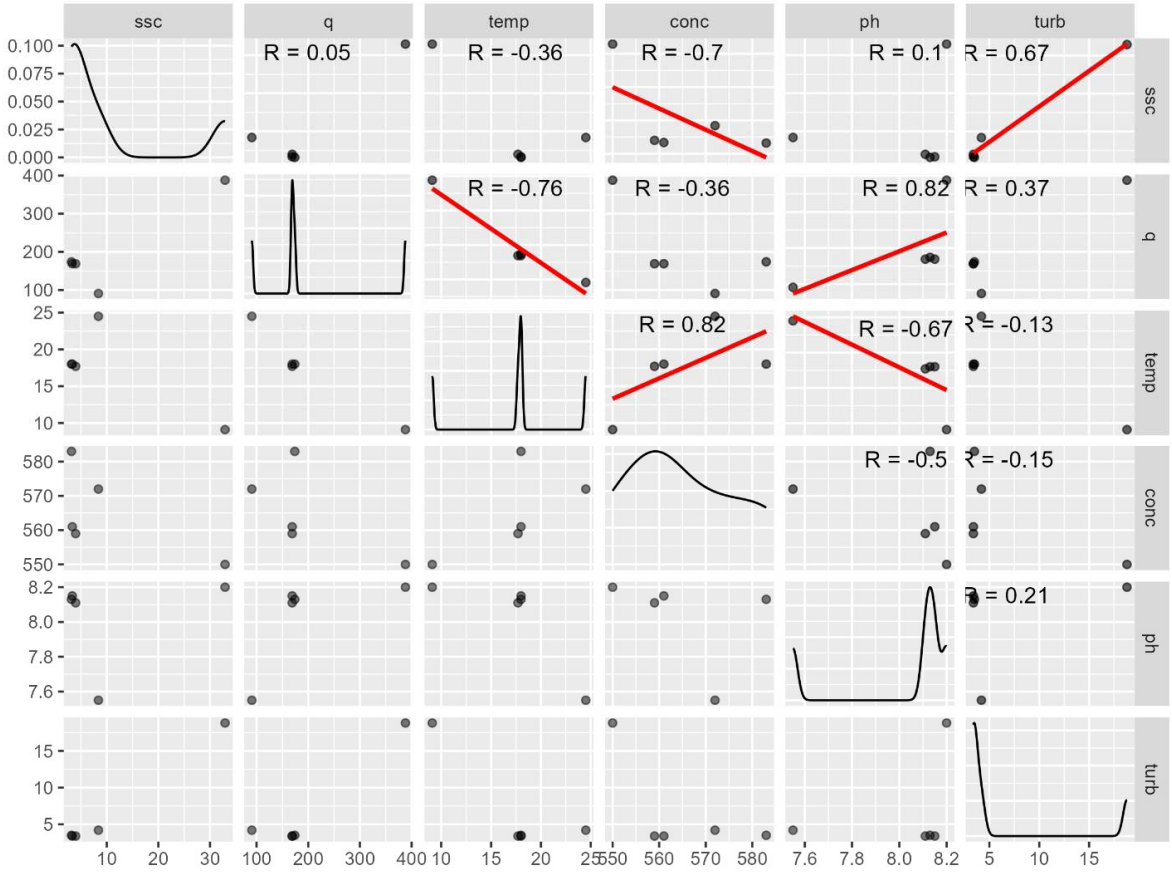


Figure SI 5 Scatter matrix for environmental variables for all five sampling days. Conc=conductivity here

Pump samples (P)

Table SI 3 MP concentrations, mass concentrations and particle size metrics for pump samples (P).

Sample	MP concentration [# L^{-1}]	MP flux [# s^{-1}]	MP mass concentration [ng L^{-1}]	Median major particle diameter [µm]	Median minor particle diameter [µm]
Feb21-P-1	0.80	311,797	573	104	58
Feb21-P-2	3.18	1,233,840	1,619	115	59
Feb21-P-3	2.90	1,123,338	2,294	102	55
Feb21-P-4	2.49	965,460	2,222	104	58
Feb21-P-5	1.17	452,447	540	100	53
Feb21-P-6	0.36	139,214	451	153	98
May03-P-1	0.17	28,710	18	81	56
May03-P-2	0.15	26,796	11	60	40
May03-P-3	0.09	15,451	9	98	48
May04-P-1	0.16	27,378	18	81	49
May04-P-2	0.16	26,972	8	60	40
May04-P-3	0.29	48,588	18	75	39
May05-P-1	0.40	68,377	126	81	40
May05-P-2	0.09	14,602	32	117	60
May05-P-3	0.01	1,927	0.5	104	38
May05-P-4	0.29	49,737	22	81	49
May05-P-5	0.24	40,459	52	120	44
May05-P-6	0.29	48,266	50	81	49
Jul28-P-1	0.80	72,400	197	81	49
Jul28-P-2	0.45	40,768	41	81	40
Jul28-P-3	0.37	33,825	109	96	53
Jul28-P-4	1.28	116,507	600	115	60
Jul28-P-5	0.98	89,544	508	128	64
Jul28-P-6	0.37	34,034	117	115	54

Relationship between number and mass concentration for pump samples

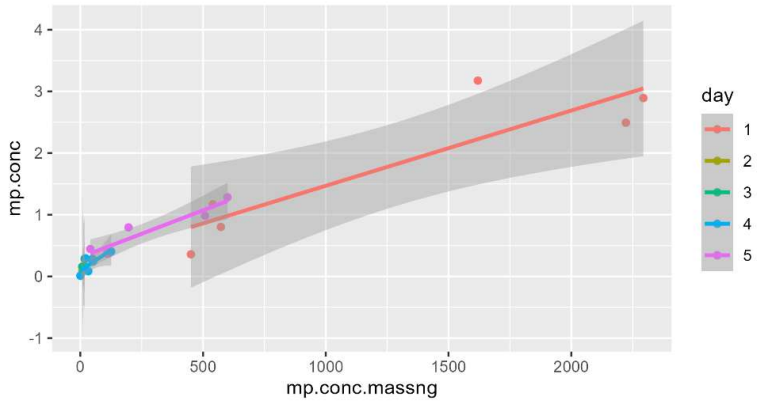


Figure SI 6 Scatterplot for MP concentration and mass concentrations of pump samples (P) and linear trendlines for subgroups of sampling day (1 = 21 July, 2 = 3 May, 3 = 4 May, 4 = 5 May, 5 = 28 July)

Relationship between MP concentration and sampling duration

The time span during which the samples were taken was ~2 hours in February and July, ~one hour on 3 and 4 May, and ~six hours on 5 May. Sampling duration was not correlated to MP concentrations overall, but for 21 February, MP concentration increased with the sampling duration (Figure SI 7). It is important to note that collinearity is implied between sampling volume and duration, and that concentration is calculated using sampling volume. But duration is better comparable with ST samples, which were measured by exposure time, not volume.

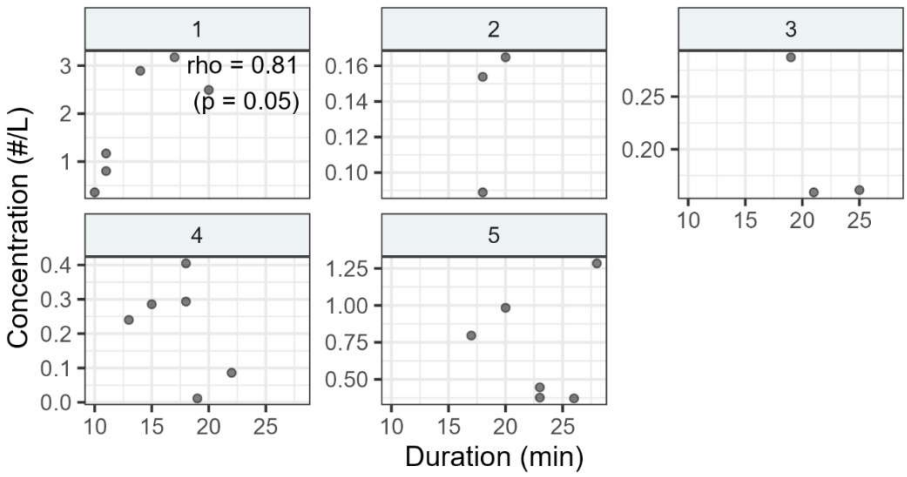


Figure SI 7 MP concentrations versus sampling duration presented in panels per sampling day (1 = 21 July, 2 = 3 May, 3 = 4 May, 4 = 5 May, 5 = 28 July), Indicated is the Spearman

correlation coefficient (rho) and p when the correlation was significant only. Pump samplings only.

MP polymer type composition across pump samples

Table SI 4 Polymer type composition of all P samples together, N= number of observation (particles), and percentage number and mass based.

Polymer type	N	Percentage (#-%)	Percentage (mass-%)
abs	6	0.5	**5**
acrylic	26	1.4	1.2
cellulose acetate	1	0.1	0.0
pa	6	0.4	0.4
pe	369	**26**	**56**
polyester	24	1.4	4
pp	900	**59**	**25**
ps	107	**7**	**5**
pu	24	1.8	1.9
pvac	6	0.3	0.4
pvc	25	1.5	1.8
sbr	3	0.3	0.7
vinyl copolymer	1	0.1	0.0

Table SI 5 Detection frequency of polymer types of all pump samples (P) and sediment trap (ST) per sampling day and detected polymer type.

Name	Day	Device	N_poly	Poly_types
Feb21-P-1	1	P	4	pe, pp, ps, abs
Feb21-P-2	1	P	9	pe, pp, ps, pvc, abs, acrylic, pu, pvac, sbr
Feb21-P-3	1	P	10	pe, pp, ps, pvc, abs, acrylic, pa, polyester, pu, sbr
Feb21-P-4	1	P	6	pe, pp, ps, pvc, pa, pu
Feb21-P-5	1	P	7	pe, pp, ps, abs, acrylic, pa, polyester
Feb21-P-6	1	P	3	pe, pp, pu
May03-P-1	2	P	4	pe, pp, ps, acrylic
May03-P-2	2	P	4	pe, pp, acrylic, polyester
May03-P-3	2	P	2	pe, pp
May04-P-1	3	P	4	pe, pp, ps, pvc
May04-P-2	3	P	2	pp, acrylic
May04-P-3	3	P	4	pe, pp, ps, polyester
May05-P-1	4	P	3	pe, pp, ps
May05-P-2	4	P	4	pe, pp, ps, vinyl copolymer
May05-P-3	4	P	1	pp
May05-P-4	4	P	5	pe, pp, ps, acrylic, polyester
May05-P-5	4	P	3	pe, pp, ps
May05-P-6	4	P	4	pe, pp, ps, polyester
Jul28-P-1	5	P	5	pe, pp, ps, pu, pvac
Jul28-P-2	5	P	7	pe, pp, ps, pvc, abs, acrylic, cellulose acetate
Jul28-P-3	5	P	5	pe, pp, ps, acrylic, polyester
Jul28-P-4	5	P	8	pe, pp, ps, pvc, acrylic, pa, polyester, pu
Jul28-P-5	5	P	8	pe, pp, ps, pvc, acrylic, pa, polyester, pvac
Jul28-P-6	5	P	7	pe, pp, ps, pvc, pa, polyester, pu
Feb21-ST-3	1	ST	5	pe, pp, ps, pvc, pu
May05-ST-1	4	ST	4	pe, pp, pvc, pa
May05-ST-2	4	ST	4	pp, pvc, acrylic, polyester
May05-ST-3	4	ST	4	pe, pp, pvc, acrylic
May05-ST-4	4	ST	1	pvc
May05-ST-5	4	ST	3	pvc, cellulose acetate, pvac
Jul28-ST-1	5	ST	6	pe, pp, ps, pvc, acrylic, polyester
Jul28-ST-2	5	ST	6	pe, pp, ps, pvc, pa, polyester

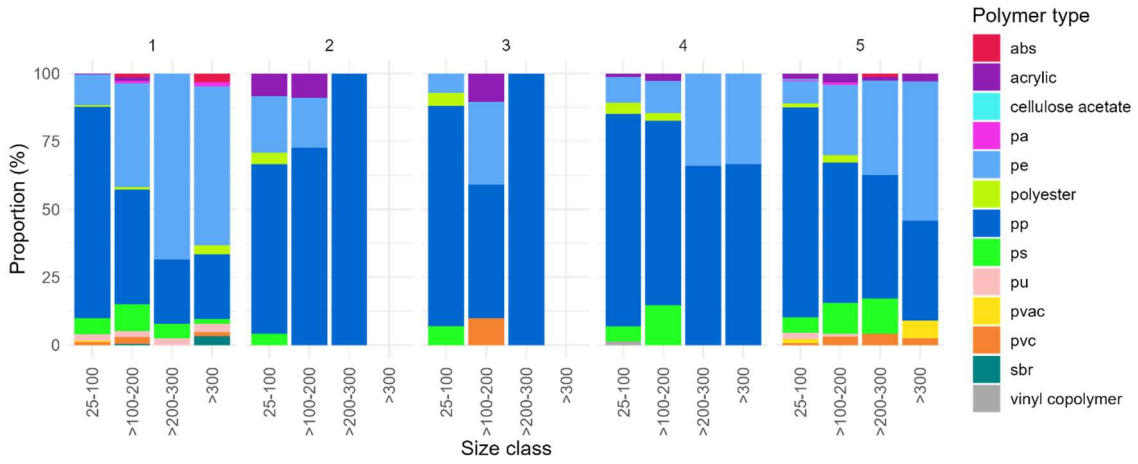


Figure SI 8 Polymer types per sampling day and by proportion per size bin. Proportion of polymer types per size bin (per bar =100%)

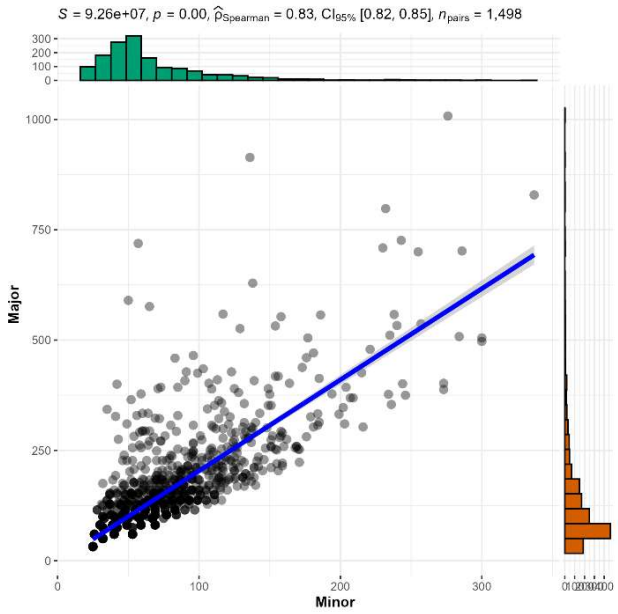


Figure SI 9 MP size distribution of all P samples, cumulated

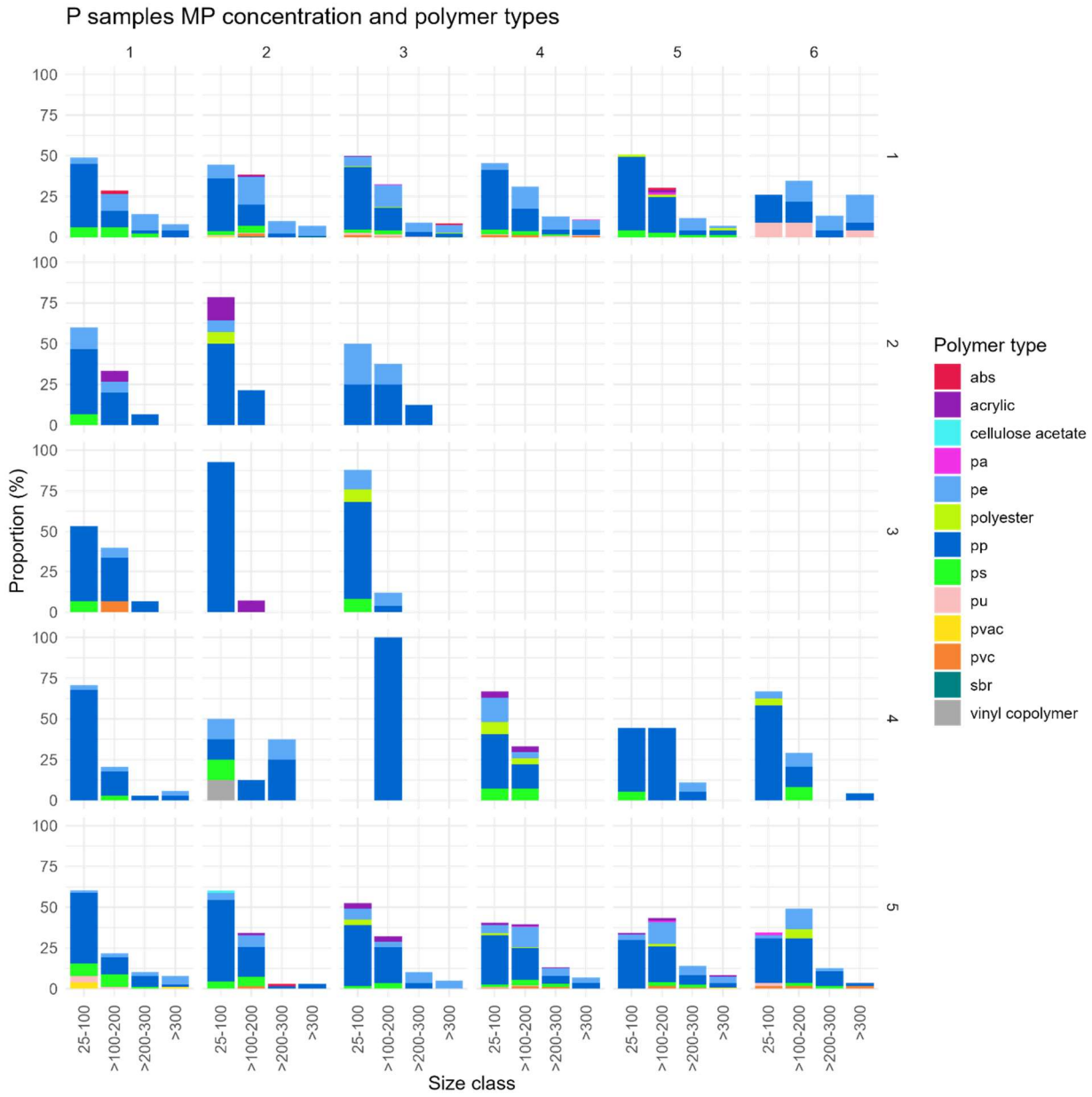


Figure SI 10 Polymer types proportions by sample number (top horizontal panels) and per sampling day (side vertical panels, 1 = 21 July, 2 = 3 May, 3 = 4 May, 4 = 5 May, 5 = 28 July). Polymer type proportion (based on MP concentration in # mg^{-1} DW) per size bin. Proportion of polymer types per sample (per panel =100%).

Sediment trap samples (ST)

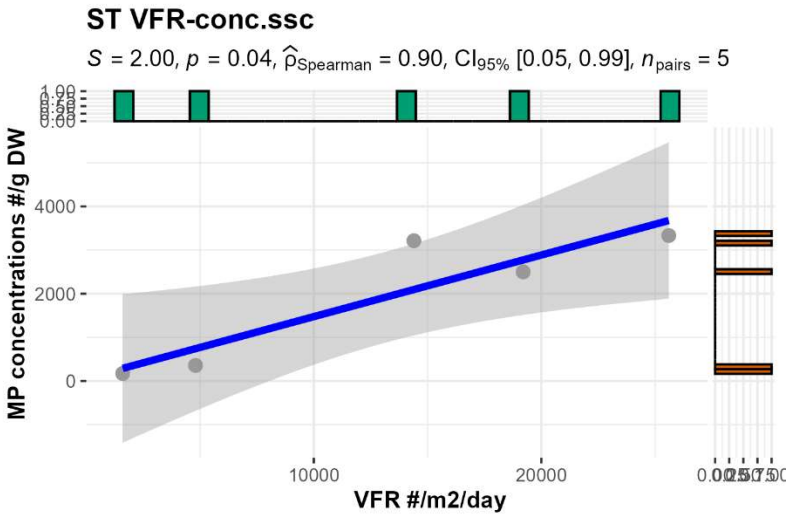


Figure SI 11 Correlation plot for ST samples of VFR ~ MP concentrations per suspended sediments for high frequency sample on 5 May 2022.

Table SI 6 Comparison of MP metrics for ST samples between days.

Campaign	Method	Median MP concentration [#g^{-1} DW]	Median MP mass concentration [µg g^{-1} DW]	Median MP vertical flux rate (VFR) [# m^{-2} day^{-1}]	Median MP vertical mass flux rate (VFR) [µg m^{-2} day^{-1}]
February	ST	-	-	108,800	73,795
May	ST (N=5)	2,500	434	14,400	2,877
July	ST	-	-	46,080	19,945

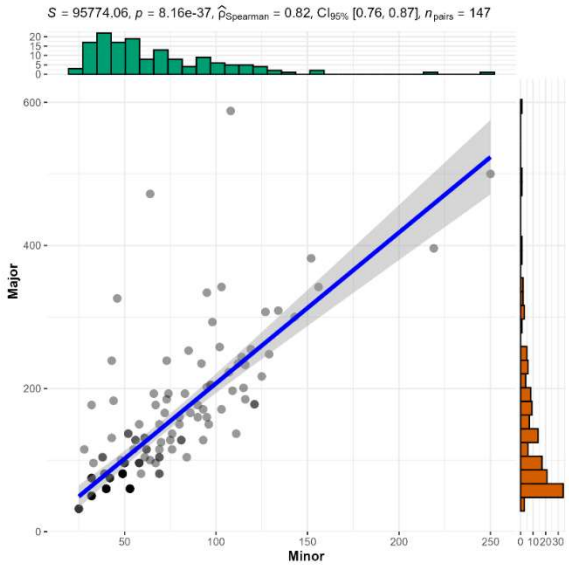


Figure SI 12 Size distribution for ST samples

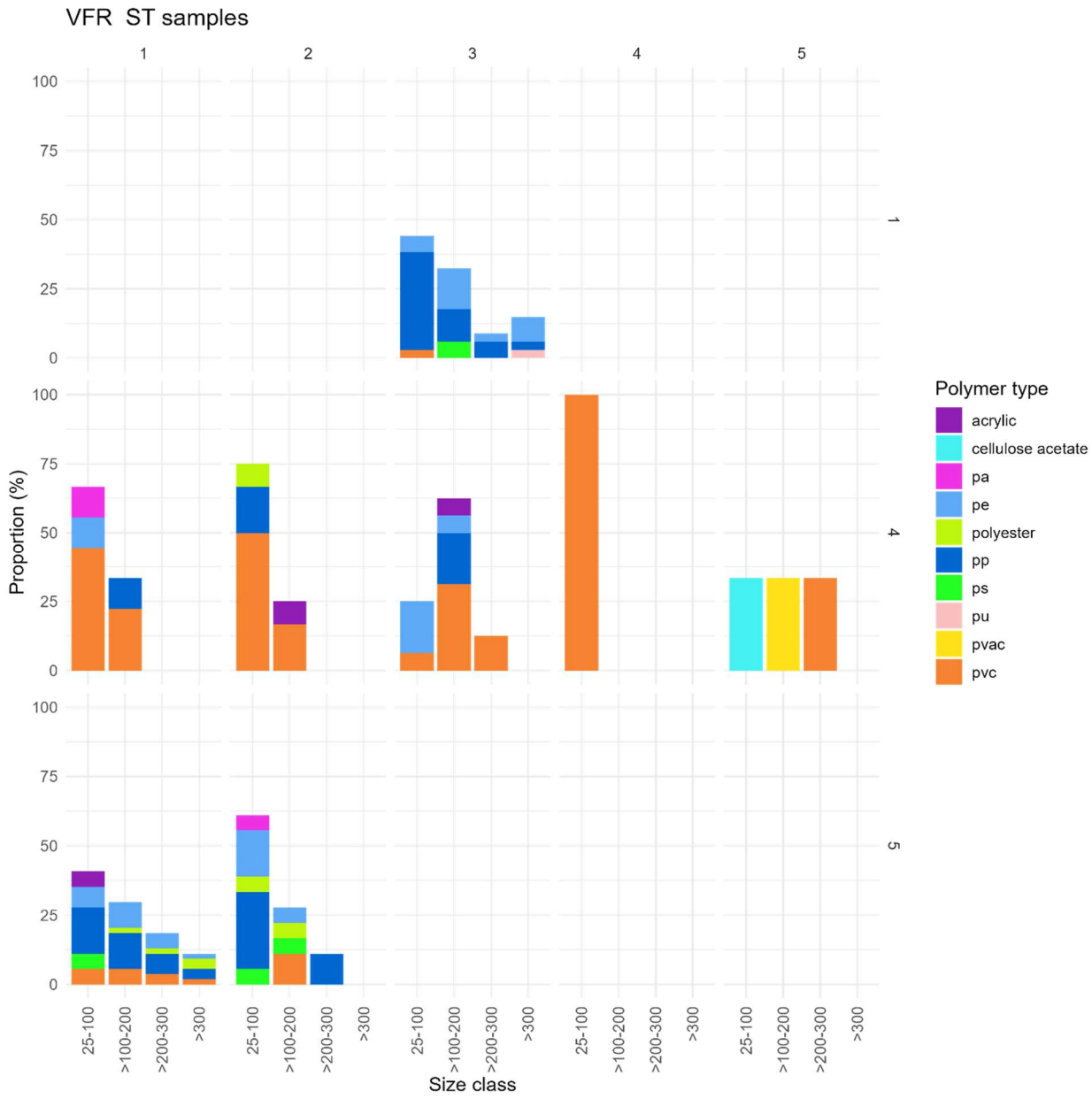


Figure 11 Polymer types proportions by sample number (top horizontal panels) and per day (side vertical panels, 1 = 21 July, 4 = 5 May, 5 = 28 July). Polymer type proportion (based on MP VFR in # m^{-2} day^{-1}) per size bin. Proportion of polymer types per sample (% per panel =100%)

Comparison P versus ST samples

To test whether the presence of polymer types differed between the two methods (P and ST), we compared presence and absence data and applied Fisher's Exact Test for each polymer type, using all sample-polymer combinations to assess whether their occurrence

differed per method. For polymers that were either always present or never detected across samples, Fisher's Exact Test was not performed (NA values in the p-value column).

Table SI 7 Fisher's Exact Test for polymer type detection frequency across sampling methods on 5 May 2022 / dataset, N=143, P = pump, ST = sediment trap

polymer	p_value	P_absent	P_present	ST_absent	ST_present
ABS	*NA*	-	-	-	-
Acrylic	0.5455	5	1	3	2
Cellulose acetate	0.4545	6	0	4	1
PA	0.4545	6	0	4	1
PE	0.2424	1	5	3	2
PP	0.1818	0	6	2	3
PS	**0.0152**	1	5	5	0
PVC	**0.0022**	6	0	0	5
PVAC	0.4545	6	0	4	1
Polyester	1.0	4	2	4	1
PU	*NA*	-	-	-	-
SBR	*NA*	-	-	-	-
Vinyl copolymer	1.0	5	1	5	0

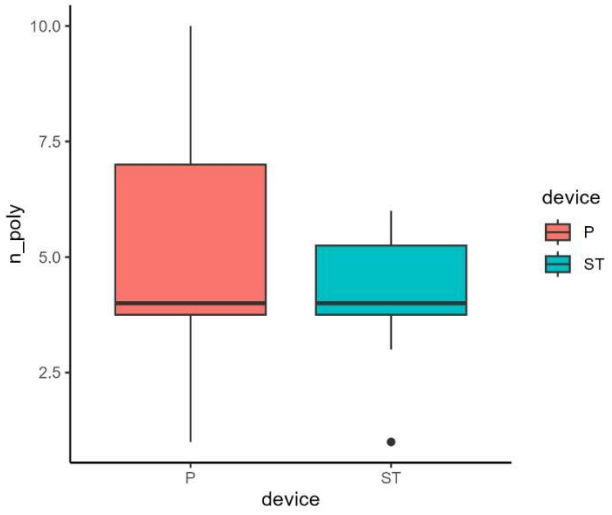


Figure SI 13 Boxplots comparisons of P and ST samples and the polymer type detection frequency (n_poly)

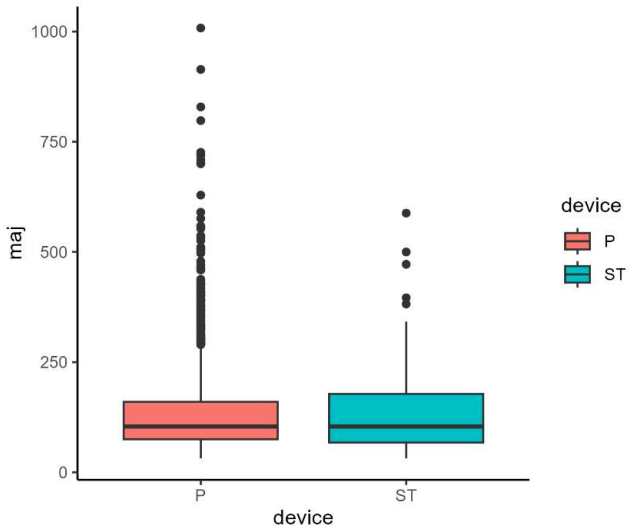


Figure SI 14 Comparison of the MP size distribution of the major particle dimension (maj) of pump (P) and sediment trap (ST) samples.

Data set for Chapter 3

Link to the database:

https://zenodo.org/records/10967114

Note: A *Corrigendum* has been submitted to the journal and is under review. The version in this thesis is corrected.

The authors regret to inform readers of a mistake in the units of microplastic mass concentration in the original manuscript and the attached database. Mass concentration units were reported incorrectly by a factor of 1,000.

The database has not yet been corrected.