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Rachid Dris

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First assessment of sources and fate of macro- and
micro- plastics in urban hydrosystems: Case of Paris
megacity

Par Rachid DRIS

Thèse réalisée au Laboratoire Eau Environnement et Systèmes Urbains, UMR MA 102

Dirigée par Bruno TASSIN et Johnny GASPERI

09 décembre 2016 à l'École des Ponts ParisTech

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Abstract

Plastic pollution in the marine environment has been widely studied since 1972, with most research being performed after 2004. Investigations into plastic pollution in freshwater and especially in urban catchments only got underway at the beginning of this decade; urban plastic pollution sources and their related fluxes in rivers remain largely unknown. Special attention should thus be paid to the level of plastic contamination in catchments exposed to severe anthropogenic pressures, notably in urban areas. This Ph.D. thesis focuses on the case study of the Paris agglomeration and its impact on the Seine River. A dual approach has been carried out with both macro- (> 5 mm) and micro- (< 5 mm) plastics taken into consideration.

The quantity of macroplastics conveyed by the Seine River was estimated by a field study and through application of a theoretical approach.

Regarding microplastics, fibers (made with synthetic as well as man-made polymers) and fragments were both evaluated in different compartments of the urban system. This study has targeted: the air compartment (indoor and outdoor air, plus atmospheric fallout), the sewer system (from washing machine disposal to WWTP influent and effluent), and the inputs during wet weathers periods, i.e. runoff and combined sewer overflows. Fiber and fragment contents were also determined in the Seine River.

This work is intended to provide relevant methodological insights into the sampling of microplastics in rivers. Two mesh size nets were tested (80 μm vs. 300 μm). The homogeneity of fiber distribution in rivers has also been verified by assessing short-term temporal and spatial variabilities. To highlight the potential impact of the Paris agglomeration, a monthly monitoring campaign at 5 sites upstream and downstream of Paris was conducted as well.

This thesis has mainly highlighted the ubiquity of fibers in all compartments. Fibers were found to be predominant in comparison with fragments across all compartments. Combined sewer overflows exhibit rather high amounts of fragments. On the other hand, the flux of microplastics in the Seine River was shown to be negligible in terms of mass relative to that of macroplastics. This study is also the first to demonstrate that the atmospheric compartment must be considered as a significant potential source of microplastics.

List of publications

The work presented in this PhD thesis was partially published in the following papers:

Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., and Tassin, B. (2016). A first overview of textile fibers, including microplastics, in indoor and outdoor environments. *Environ. Pollut.* 221, 453–458

Dris, R., Gasperi, J., Saad, M., Mirande, C., and Tassin, B. (2016). Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? *Mar. Pollut. Bull.* 1–2, 290–293.

Dris, R., Imhof, H., Sanchez, W., Gasperi, J., Galgani, F., Tassin, B., and Laforsch, C. (2015). Beyond the ocean: Contamination of freshwater ecosystems with (micro-) plastic particles. *Environ. Chem.* 12, 539–550.

Dris, R., Gasperi, J., Rocher, V., Saad, M., Renault, N., and Tassin, B. (2015). Microplastic contamination in an urban area: a case study in Greater Paris. *Environ. Chem.* 12, 592–599.

Gasperi, J., Dris, R., Bonin, T., Rocher, V., and Tassin, B. (2014). Assessment of floating plastic debris in surface water along the Seine River. *Environ. Pollut.* 195, 163–166.

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List of abbreviations

ATR - Attenuated Total Reflectance

CA - Cellulose acetate

CARE - Asian center for water research

CSO - Combined sewer overflow

EDS - Energy Dispersive X-Ray Spectrometer

FPA - Focal plane array

FTIR - Fourier Transform InfraRed

GDP - Gross domestic product

GIP - Public interest grouping

HCMC - Ho Chi Minh City

HDPE - High-density polyethylene

ICMPE - Paris-Est institute of Materials Chemistry

IFREMER - French research institute for exploitation of the sea

INSS - National institute of statistic and economic studies

LDPE - Low-density

LDCM - Detection, sensors and measurements Laboratory

PA - Polyamide

PC - Polycarbonate

PE - Polyethylene

PES - Polyester

PET - Polyethylene terephthalate

PP - Polypropylene

PS - Polystyrene

PUR - Polyurethane

PVC - Polyvinyl chloride

RIC - Resin identification code

SDS - Sodium dodecyl sulfates

SEM - Scanning electron microscopy

SIAAP - Greater Paris inter-departmental sanitation consortium

SPI - Society of the plastics industry

TOC - Total organic carbon

WWTP - Wastewater treatment plants

Introduction



The great wave of Kanagawa made initially by the artist Hokusai, updated by Bonnie Monteleone as if it was made today

Worldwide plastic production has experienced exponential growth since the beginning of the 1950's. With an average annual increase on the order of 5%, the output of plastics has been rising faster than the global population, indicating the increasingly frequent use of plastics in greater numbers of applications. Some 40% of this production is intended for packaging purposes (PlasticsEurope, 2015), i.e. short life products, thus leading to huge quantities of waste and a major global environmental issue. Plastics are included in fiber production, alongside other natural (cotton) or artificial (rayon) polymers. More precisely, plastic polymers account for 60% of the world's fiber production (Food and Agriculture Organization of the United Nations, International Cotton Advisory Committee, 2013).

Plastic debris in the oceans has now become ubiquitous. While the first warnings appeared in the scientific literature in the early 1970's (Carpenter and Smith, 1972; Carpenter *et al.*, 1972), it would take until 1997, when oceanographer Charles Moore discovered the "Great Pacific Garbage Patch", for global concerns over plastics in our oceans to be raised.

Plastic debris comes in various shapes and presents a continuum of sizes. In 2004, a paper published by Thompson drew attention to the presence in the environment of much smaller plastic particles, so-called microplastics (Thompson *et al.*, 2004). These particles may be shaped like fragments, spheres, pellets, films or fibers. Over the past decade, microplastics have received considerable attention by both the scientific community (Figure 1) and the global media. In 2008, they came to be defined as plastic particles smaller than 5 mm (Arthur *et al.*, 2008). Since this definition is the most widely accepted and used by the scientific community, it has been adopted in this manuscript. In contrast, macroplastics are defined as plastic debris whose smallest dimension remains greater than 5 mm.

In addition to its aesthetic nuisance, plastic debris exerts an adverse environmental impact. The risks generated by such debris are twofold. First, the smaller particles may be ingested by a vast array of species, causing physical harm most often related to a disruption of the digestive system (blocking of intestinal tract, false sensation of satiation, etc.). The second category of risks pertains to the fact that these particles carry a "cocktail of chemicals" they either transport over long distances or release inside an organism after being ingested. Such chemicals are introduced into the plastic polymers during production or may adsorb to them once in the environment.

In examining the scientific literature regarding this recent issue, a dramatic increase in the number of publications focusing on plastic debris can be observed over the past several years (Figure 1). This trend is even more pronounced, when considering microplastics alone, thus acknowledging the significant increase in scientific efforts devoted to this topic. From the time this study started (2013), the number of publications has more than doubled.

Over the last ten years, knowledge of the sources, fate, occurrences and dynamics of these particles, as well as their interactions with biota and pollutants, has been constantly expanding and scientific community opinions have often shifted. Some initial statements were later challenged, e.g. the potential translocation of microplastics into organisms. Methodologies have also evolved tremendously, and the first protocol presented in Thompson's paper has been considerably improved since. Similarly, for a long time, visual observation was the most widely used method to identify plastic particles, whereas chemical characterization with spectroscopic methods is now regularly employed (Hidalgo-Ruz *et al.*, 2012).

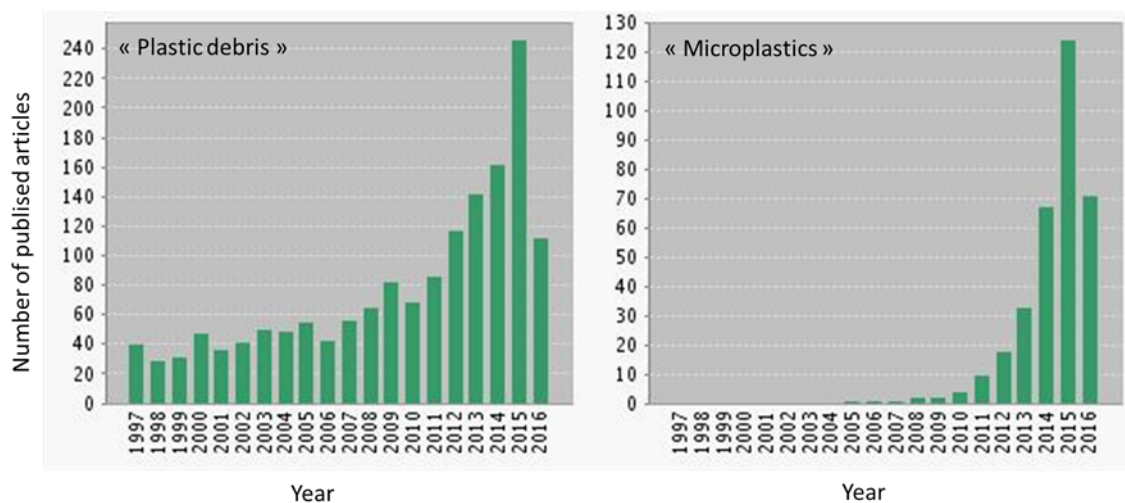


Figure 1: The number of articles referenced in Web of Knowledge per year using the keywords "plastic debris" and "microplastics" to direct the search. These graphs were produced on August 10, 2016.

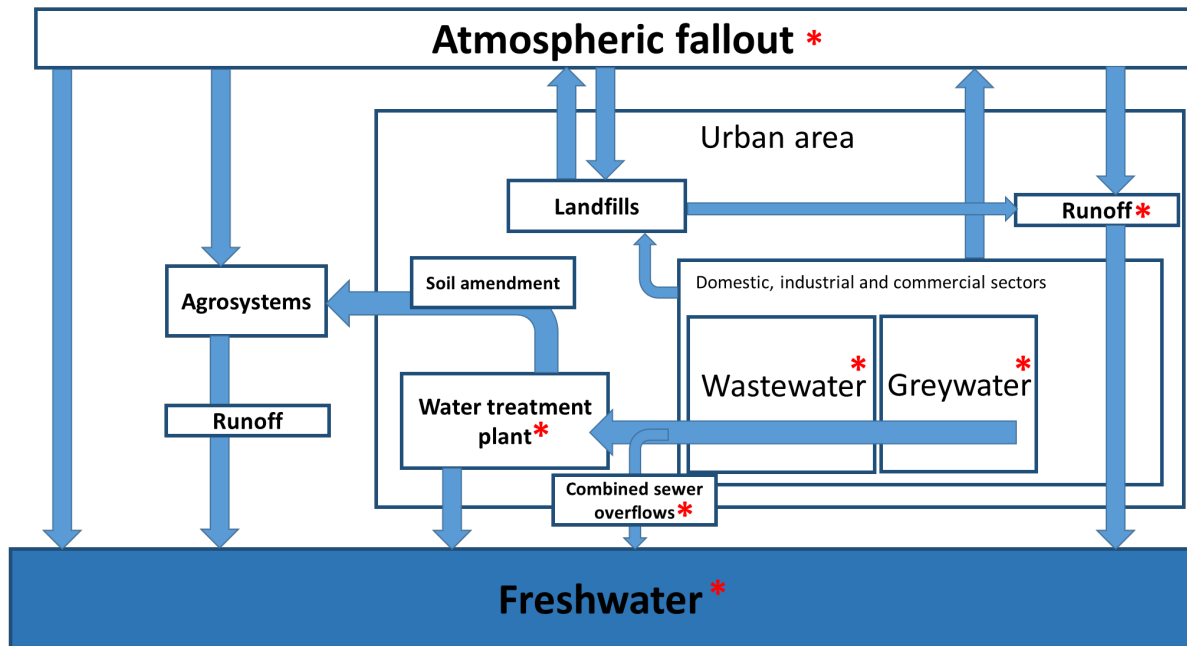
The body of scientific work related to plastic pollution (both macro- and microplastics) is mainly oriented towards marine environments. Surprisingly, the focus on plastic pollution in continental environments has been quite limited, although it is generally assumed that 80% of the plastic pollution detected in marine environments originates from a terrestrial source (UNEP, 2009) (even if this widely cited figure has been very poorly substantiated and

documented). At the beginning of this PhD thesis in 2013, the sources and dynamics of plastic debris in watersheds and freshwater were only sporadically documented. In 2011, a paper had already alluded to the fact that washing machine effluent constitutes a major source of textile fibers (Browne et al., 2011). Consequently, we would expect that major conurbations are responsible for high fiber inputs into the environment. Moreover, an increasing proportion of the world's population lives in cities (54% in 2014, 66% forecast in 2050). Paradoxically, the dynamics of fibers and plastics in urban catchments and hydrosystems are practically unknown; their fate, transfer routes and processes in continental water have yet to be determined.

The aim of this work therefore is to provide an initial comprehensive analysis of the sources and fate of macro- and microplastics in an urban environment: the Paris megacity was chosen. Mainly referred to as the Paris agglomeration in this manuscript, this megacity is one of the world's 40 largest with a population of over 10 million (INSEE, 2013). The Paris agglomeration is crossed by the Seine River, whose catchment drains an area of approximately 32,000 km² from the river's headwaters to Paris. This catchment combines intense anthropogenic pressures with a very limited dilution factor due to the low average flow (350 m³.s⁻¹ in Paris).

The Paris megacity in fact exerts a dramatic impact as regards micropollutants on the river (Gasperi, 2013). To provide a comparison and gain a greater perspective, another megacity with very different dynamics, namely Ho Chi Minh City, was also investigated, albeit in far less depth. The results from this second megacity will be commented only briefly.

Offering new and original data is a major objective of this PhD thesis, as are assessing the inputs and pathways of plastic pollution in an urban environment and estimating the downstream flow of this contamination. A similar approach had previously been used in other works related to the dynamics of emerging contaminants in Greater Paris (Bressy, 2010; Cladière, 2012). One output of these prior works was a generic depiction of the sources and transfer routes of pollutants in urban environments. This representation has been adapted in to plastics and microplastics (Figure 2).



* Compartments studied in this PhD thesis

Figure 2: A schematic diagram showing potential fiber and microplastic pathways and inputs into freshwater in an urban context.

Plastic originating from urban activities will reach all three environmental compartments, namely: atmosphere, water, and soil. Industrial emissions, landfill and waste incineration, particle re-suspension and other anthropogenic causes (traffic, buildings, urban infrastructure, etc.) are all potential sources of plastic in the atmosphere. The textiles worn by the population might also emit fibrous microplastics into the atmospheric compartment. These particles would subsequently deposit as atmospheric fallout and may reach the aquatic compartment through rainwater and runoff. Plastics may also reach the aquatic compartment directly due to uncivil or informal behavior, e.g. littering, in the form of macroplastics, after which they would fragment and release microplastic particles while in the freshwater. The urban water system drained by combined or separate sewers also serves as a major point of entry for plastics to be considered. Lastly, soils could be contaminated through either atmospheric fallout or soil amendment, which is often carried out with sludge stemming from wastewater treatment processes. These microplastics will potentially reenter the aquatic compartment by way of runoff. Practically nothing is known about either the behavior of plastics in these compartments or the dynamics within or between them, hence the need for further investigations.

In this context, this manuscript presents the main results of a three-year investigation according to an approach based on this conceptual depiction. A number of compartments have been considered (Figure 2). Moreover, due to the fact that plastics in the environment display a continuum of sizes, a complementary approach has been adopted for this work. Both macroplastics (> 5 mm) and microplastics (< 5 mm) have been studied. Moreover, the fibers and microplastic fragments were considered separately. This manuscript has been structured into 6 chapters, organized as follows:

- **Chapter 1: Review of the literature on plastic pollution**

The first chapter is devoted to a literature review. It begins by presenting definitions and key figures for plastic materials. Since fibers are a significant type of plastic yet often not included in global figures, a focus on fibers is presented.

The environmental issue will then be introduced and the main articles dealing with the definition of macro- and microplastics, their types, sources, impacts and occurrences in the marine environment will be briefly discussed. As this PhD thesis is investigating plastic pollution in a continental context, a detailed review of previous studies assessing continental contamination will be provided. Results will be presented and methodologies described. The articles exploring urban inputs will also be reviewed.

- **Chapter 2: Description of the study sites and methods used to quantify and characterize plastics**

This chapter has two main purposes. First, it will present the Paris agglomeration and Seine River, as well as Ho Chi Minh City. In a second section, the methodologies employed to analyze microplastics will be discussed. While the specific sampling procedure changes among the compartments, the subsequent steps (organic matter removal, separation from mineral fraction, observation and characterization) are common to all samples and therefore included in this chapter in order to avoid redundancy.

- **Chapter 3: Estimation of macroplastic debris in urban rivers**

Chapter 3 will focus on the case of macroplastics. These debris surpass microplastics in terms of both volume and mass; consequently, they represent the predominant mass flow of plastic

material in rivers. Given that the total mass of plastic entering oceans from waste generated on land is unknown, estimating the macroplastic masses flowing into rivers is crucial.

In this study, the quantity of plastics flowing into the Seine River has been assessed. Two distinct approaches have been pursued. The first consists of basing estimations on a field study. An opportunistic sampling approach has relied on a boom net network previously installed by SIAAP (Greater Paris Inter-Departmental Sanitation consortium). A similar approach was conducted in Ho Chi Minh City. The aim here is to provide a comparison between cities with different waste management systems and different economic contexts. While no boom network exists in Ho Chi Minh City, various companies do proceed on a daily basis to the manual collection of garbage floating in various canals.

In parallel, a more theoretical approach has been implemented to estimate the plastic quantity that escapes from the waste management system and potentially ends up in surface water. A paper in 2015 provided such an estimation for 192 countries (Jambeck *et al.*, 2015). Though this approach was global and had to make use of some rather rough extrapolations, its method has been reapplied here at a more local scale. The theoretical input of plastic will then be compared to field study results.

- **Chapter 4: Sources of microplastics in an urban area**

While microplastics are small and do not represent a large mass, they are clearly predominant in numbers. Assessing the levels of microplastics in the environment is a key criterion that will serve to estimate the ingestion and effect risks for biota. Chapter 4 will address a critical issue, namely the pathways of these contaminants in a city.

In urban environments, many sources and inputs can be considered for microplastics. This chapter will be based on the systemic approach conceptualized in figure 2. As an initial step, different compartments will be studied in this section.

Fiber concentrations in both indoor and outdoor air are being investigated for the first time. To develop a complete overview for fibers including microplastics in the indoor environment, fibers have also been studied in dust fallout and settled dust.

Atmospheric fallout has been considered. While wastewater treatment plants (WWTP) are considered to be chiefly responsible for fibers in freshwater, fibers originating in the atmosphere could still account for a large proportion and must therefore be examined. This source of fibers and microplastics will be explored for the first time herein. As a direct consequence, fiber microplastics can also be found in runoff water. This potential input into rivers will also be assessed.

Fibers and microplastics have been evaluated in washing machine effluent for their potential river input. More specifically, greywater, wastewater, settled water and WWTP disposal have all been investigated, in addition to considering combined sewer overflows (CSO).

Since the study of microplastics in the air is unprecedented, this pilot study proceeded with a yearly monitoring for both indoor environments and atmospheric fallout. However, due to the fact that microplastics analyses are time-consuming, only a few samples have been considered for the other compartments. It was decided not to focus on any single compartment but instead derive an idea of the most significant pathways to fill in the many gaps in knowledge that are present. This work is in fact highly innovative by virtue of studying various inputs and comparing them in order to generate a more precise understanding of the sources.

- **Chapter 5: Microplastics in urban rivers**

The concentrations of fibers and microplastic fragments will be assessed in this chapter. Regarding the novelty of the topic for river environments, a number of crucial challenges related to the sampling methodology will also be addressed.

Manta trawls or neuston nets with a mesh size of approx. 330 μm have been used in studies focusing on microplastics in rivers (McCormick *et al.*, 2014; Moore *et al.*, 2011; Yonkos *et al.*, 2014). This approach probably represents a transposition of typical microplastic sampling practices in marine environments (Hidalgo-Ruz *et al.*, 2012). Other types of nets with various mesh sizes have also been used to sample plastic debris in rivers, including: < 1 mm mesh size stream band samplers and hand nets (Moore *et al.*, 2011), eel fyke nets (Morritt *et al.*, 2014), and 500 μm mesh size stationary driftnets (Lechner *et al.*, 2014). Moreover, the sampling methodology (position, surface vs. deep water layer, center vs. left and right banks) differs depending on the study. Homogeneity through the water cross-section has not yet been

demonstrated. While it can still be assumed that low-density plastics float in a marine environment and lakes, current conditions in rivers make this assumption less obvious. A portion of this work program therefore has been aimed at deriving insights about river water sampling. Along these lines, a number of questions had to be addressed.

Two different mesh sizes were used (80 μm in the form of a plankton net, and 300 μm in the form of a manta net and plankton net). This set-up will compare sampling using two mesh sizes and highlight the benefits and drawbacks of each mesh size.

Short-term temporal variations in fiber concentration can occur. This work has verified how such variations would affect the representativeness of one-time samples. The vertical and horizontal concentration profiles have also been investigated to yield a better understanding of the fiber distribution in river cross-sections and justify the pertinence of localized sampling of buoyant water.

A long-term spatial (upstream and downstream of Paris) and temporal (19-month) variation was carried out in the form of a monthly monitoring for the purpose of generating an idea of the fiber quantities flowing into the Seine River within the Paris conurbation. On the other hand, snapshot sampling campaigns have been conducted in order to quantify fragments in the Seine River and provide a comparison with fibrous contamination levels. Also, a comparison with Ho Chi Minh City has been performed to assess freshwater contamination in a context with practically no wastewater treatment.

- **Chapter 6: Conclusion, research needs and outlook**

The final chapter will first discuss the main findings of this PhD thesis. The fluxes and inputs obtained across the various chapters will be compared and described. Next, the main issues regarding aspects addressed throughout this thesis will be debated. In closing, the main gaps in knowledge that this study has helped to highlight will be identified in detail, and the prospects for further work will be proposed.

Chapter 1: Review of the literature on plastic pollution



<http://oceanlegacy.ca/>

“Water and air, the two essential fluids on which all life depends, have become global garbage cans...”

Jacques Yves Cousteau

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I. General information on plastics

1. Definition and properties

It is very difficult to produce an accurate and adequate definition of what is considered a plastic material. The word “plastic” existed long before the first “modern” plastic and describes anything that can be easily molded or shaped. Derived from the Latin “*plasticus*” and the Ancient Greek “*πλαστικός*” (*plastikos*), the term literally means “capable of being molded”. In more recent times, plastic materials have often been defined on the basis of their physical properties, given their specifications as lightweight, resistant, durable while offering efficient thermal and electrical insulation (Thompson *et al.*, 2009).

An alternative definition can also be provided by examining the chemical nature of these materials. In chemistry, plastics are defined as synthetic organic polymers derived from the polymerization of monomers extracted from oil or gas (Saunders, 2013). This general definition is open to debate however since celluloid is considered as the first man-made plastic material even though its chemical composition consists essentially of nitrocellulose (Brydson, 1999). Another example would be biobased plastics: some biobased polymers only differ from oil-based polymers by their isotopic composition. Despite their renewable origin, this category of materials must still therefore be considered as plastics.

Yet this definition, based on both industrial and chemical parameters, leads to classifying plastics relative to their polymeric structure and underlying monomers. Polymers consist of a repetition of the same element, a monomer, in the form of chains. Plastics are then manufactured using these monomer chains. Differences in the physicochemical characteristics of these chains create differences in plastic polymer properties and end uses:

- Polymer chain length influences material strength. The longer the chain, the stronger the polymer. Polymer strength can be quantified as the amount of force needed to be applied before the chain breaks.
- The presence or absence of polar side groups also influences strength. Polar side groups that lead to hydrogen bonding increase the attraction between chain polymers, thus strengthening the polymer.

- The cross-linking phenomenon involves covalent bonds that may exist between the polymer chains, making the polymer harder and more difficult to melt.
- The chains can feature more or less intense branching. Straight and unbranched chains result in denser and stronger polymers.

These structural characteristics provide the plastic polymers with distinct physical properties. For instance, their densities differ, oscillating between 0.9 and 1.45 g.cm⁻³ (Figure 3). The same polymer, e.g. polyethylene (PE), can exhibit quite different properties depending on its branching. Low-density polyethylene (LDPE) has long-chain branching, whereas high-density polyethylene (HDPE) contains mostly straight chains and is therefore stronger in addition to being more dense.

Thermal properties are also an important feature to consider as they enable placing plastics into one of two categories: thermosetting and thermoplastic resins. Thermosetting resins are thermally hardened and cannot become soft again. On the other hand, thermoplastic resins can be re-softened by heating. They are used in industry in pellet form and capable of being melted and re-pelletized for reuse and recycling applications.

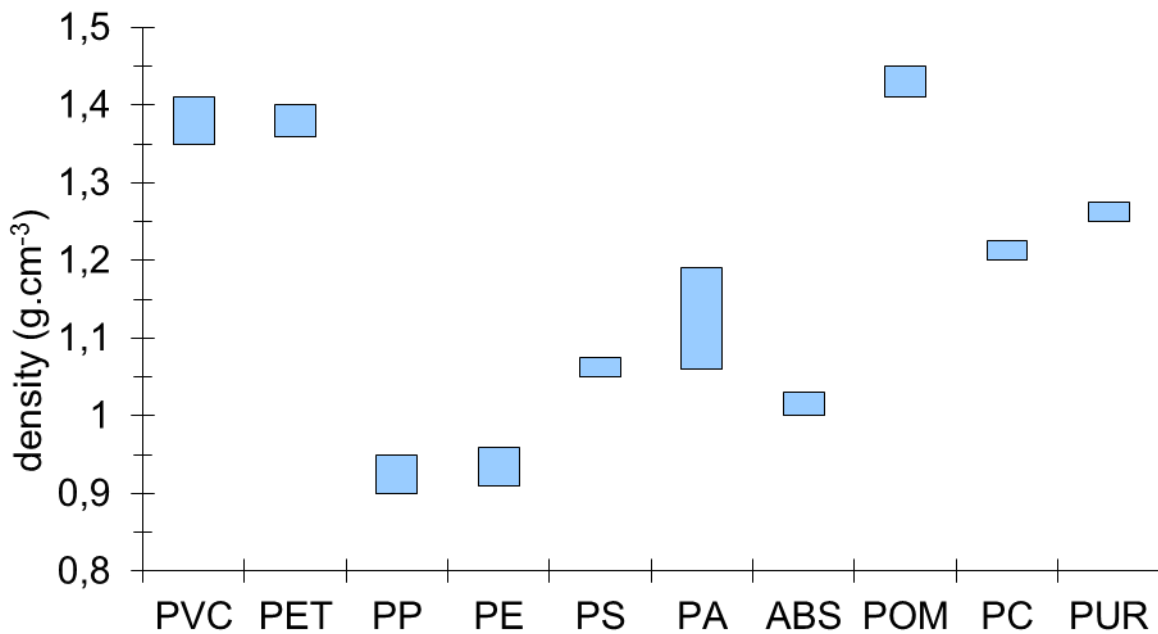


Figure 3: Densities of some of the most widely used plastic polymers (Brydson, 1999).

2. Main plastic polymers

The plastics industry employs the resin identification code (RIC) in order to define and categorize plastics; this protocol facilitates the efficient recycling of plastics by helping separate them upstream of the melting process. This system was first introduced by the Society of the plastics industry (SPI) (PlasticsIndustry, 2015). The description of these categories presented below has been based on information collected from the SPI website combined with information on polymers extracted from the book “Plastics Materials” (Brydson, 1999). Below are displayed the seven pictograms of the code numbers associated with plastic materials used in industry (Figure 4).

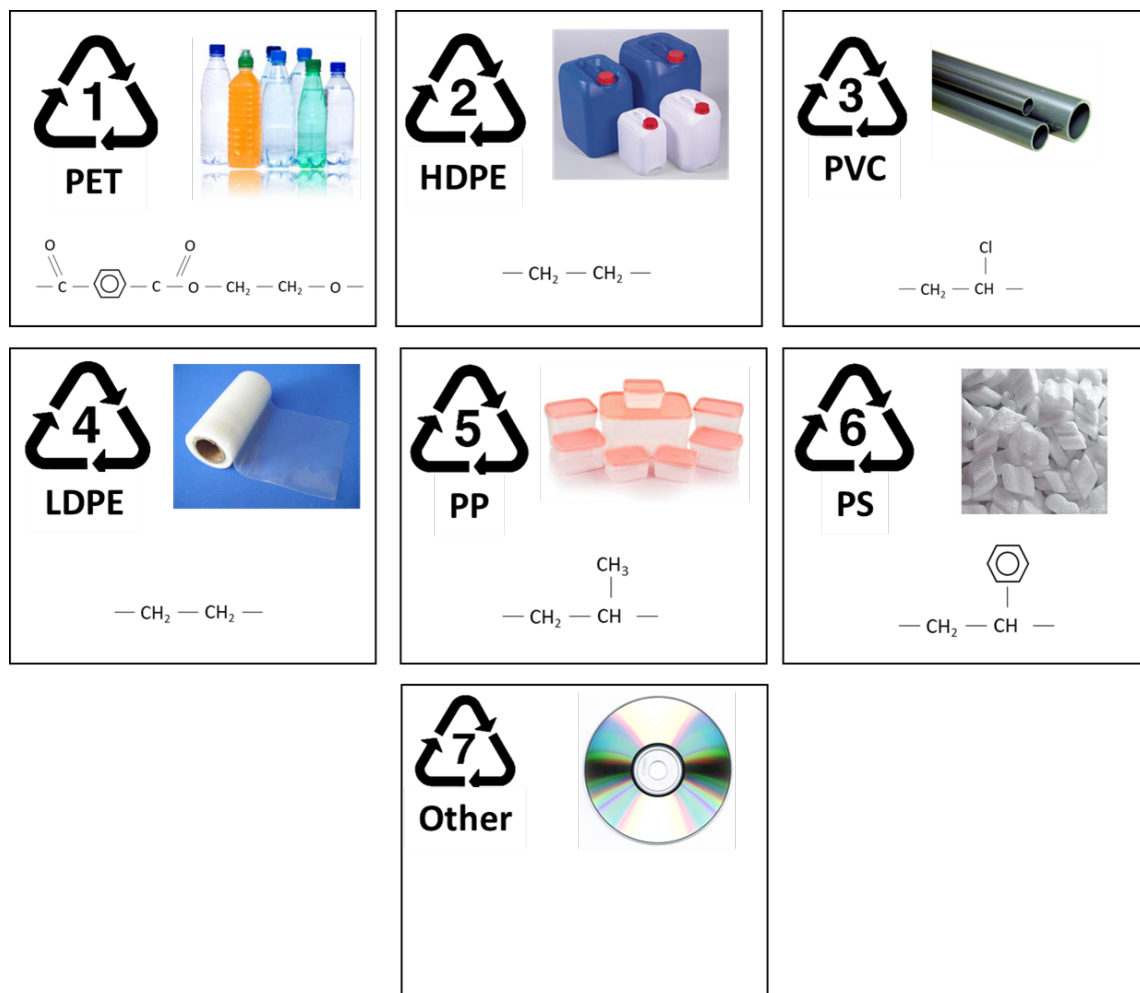


Figure 4: The code numbers for the various types of plastics established by the SPI, along with the molecular structure of the monomers and use examples.

Polyethylene terephthalate (PET) is a polymer composed of a linear polyester (PES). Polyesters are highly diverse plastic polymers with the ester (-COO-) link in common. This link

only comprises a small part of the chemical structure of the molecules. Though the first polyester resin was prepared in 1883, PET would not be patented until 1941. PET forms the basis of synthetic polyester fibers and therefore is commonly used in clothing, ropes and carpet fibers. The application of PET in beverage bottles has also become quite widespread. As PET is a thermoplastic, items containing PET are recyclable.

Polyethylene (PE) is the simplest organic polymer given that it corresponds to a linear polymer of the monomer ethylene. PE was first commercialized in 1933 and has been widely appreciated since then due to its low price, excellent electrical insulation properties, strong chemical resistance, ease of processing, toughness, flexibility and, in thin films, transparency. High-density polyethylene (HDPE) is used, for example, in electrical insulation, bottles and toys while low-density polyethylene (LDPE) is mainly found in film wrap and plastic bags.

Polyvinyl chloride (PVC) is a polymer of vinyl chloride, most often obtained by reaction with oxygen and hydrogen chloride over a copper catalyst. The polymerization of vinyl chloride, when exposed to sunlight, was first reported in 1872. PVC is a colorless rigid material with very limited stability. For these reasons, other ingredients and additives are required to transform it into a useful plastic material. It then becomes possible to produce a wide range of domestic and industrial items, including rigid piping and window frames.

Polypropylene (PP) results from the polymerization of propylene; this process only dates back to 1954 but by 1957 its commercial use had become widespread. PP is normally tough and resilient. Among the plastics presented herein, it has the lowest density. PP is extensively used in packaging, fibers (i.e. textiles, ropes, carpets) and films.

Polystyrene (PS) has been commercialized since the early 1930's; it first garnered interest thanks to a host of desirable characteristics, such as low cost, transparency, good electrical insulation properties, rigidity, low water absorption and ease of molding. This aromatic polymer exists in either solid or foamed form and is used in a wide variety of products, e.g. protective packaging, food containers and building materials.

Others (O) is the category comprising plastics manufactured from an array of diverse materials not necessarily fitting into one of the other categories. An "O" designation corresponds to products made with a plastic other than the six common ones listed above, like polyamide

(PA) or polycarbonate (PC), or else to copolymers composed of more than a single monomer. Thermosetting plastics like polyurethane (PUR) are included in this "O" category.

Bioplastic and natural plastics are also sometimes indicated by RIC code number 7. The word bioplastic on its own is ambiguous: the IUPAC (International Union of Pure and Applied Chemistry) recommends using the more accurate term of "biobased plastics" rather than "bioplastics" (Vert *et al.*, 2012). A wide range of materials can be labeled a "bioplastic", which in fact constitutes any plastic containing carbon that has been derived from renewable biomass as opposed to carbon derived from fossil resources. Some of the most widely used biobased materials are: corn, potatoes, rice, palm fibers, sugar cane, and wood cellulose. Biobased plastics include biodegradable materials like polyhydroxybutyrate (PHB), which is fully biodegradable. However, the majority of synthetic polymers (PP, PE, PET, PA, etc.) can be synthesized from sugars or vegetable oils, in forming plastics with the exact same chemical structure as if they had been synthesized from fossil fuels. The only difference would lie in the isotopic fractionation of the carbons (Quarta, 2013). These biobased plastics are not biodegradable. Consequently, let's keep in mind that biobased plastics are not always environmentally friendly. Those containing variable proportions of both renewable and petrochemical carbons are also labeled as "biobased plastics".

3. *Plastic additives*

Typical plastic items are not virgin polymers. As a matter of fact, many different additives are incorporated into them; these may be just added “onto” the material or actually incorporated “into” it, thus becoming chemically bound in the polymers. A detailed report was published in 2013 presenting the functional additives and dyes generally used within the industry (Hansen *et al.*, 2013). Some relevant data from this report will be briefly presented below. The aim of this section is not to exhaustively present all the additives and molecules potentially present in plastic polymers, but merely to highlight the fact that plastic materials are always associated with a “cocktail of chemicals” capable of migrating during the life cycle of a plastic object.

Plasticizers are substances added into certain plastics to enhance their flexibility. In the plastics industry, these additives are often introduced in very large proportions (between 10% and 70% of the weight of the virgin plastic material). Phthalates are the most popular category of plasticizers. One of the most widely plasticized plastics is PVC. Cellulose plastics, like cellulose acetate, also typically contain plasticizers.

Flame retardants are added to plastics when their material specifications call for use under certain fire standards (cables, transport, buildings, carpets, etc.). They will also typically be found in plastics exposed to high temperature (hair dryers, electronics, etc.). They may be either organic or inorganic. Organic brominated molecules (e.g. polybromodiphenylethers) are often considered the most dangerous flame retardants for their human health impacts, capable of accounting for up to 50% of the weight of the virgin plastic material.

The other functional additives are used in smaller amounts (between 0.1% and 3% of the virgin plastic material by weight). Biocides are primarily used in PVC and foams; they are either mineral (arsenic) or organic (triclosan). Antioxidants and UV stabilizers are phenolic compounds used in LDPE and HDPE, among other applications. Metals are also often used as heat stabilizers, i.e. mainly lead, tin, barium, cadmium and zinc compounds. Stabilizers are used to increase the mechanical resistance of plastics to aging.

Slip agents are added to reduce the coefficient of friction of plastics while maintaining their optical properties such as transparency. Conventional slips are based on unsaturated acid

amides, most commonly oleamide and erucamide. Along with stabilizers, they are the most extensively used additives in packaging film (PE and PP).

In addition to functional additives, other chemicals stem from plastics manufacturing. During the production process, curing agents are employed. Polymer curing is the reaction introduced to convert molten liquid resins into insoluble solids. This reaction is catalyzed with curing agents like sulfur, which will remain held in the plastic material structure. Similarly, blowing agents contribute to the foam structure of plastics during the production process.

Dyes are also widely used in the plastics industry; they may be either organic or inorganic (cadmium, lead and chromium-based compounds). Dyes are highly appreciated for marketing purposes, in coloring plastic objects according to specifications; they can represent up to 10% of the virgin plastic weight.

Fillers are not introduced into plastic materials to achieve a specific property, but instead simply to lower production costs. Low-cost fillers will in fact reduce the consumption of more expensive materials by constituting up to 50% of the weight. As opposed to the other compounds listed above, fillers are generally non-hazardous and natural. Calcium carbonate and wood powders are mainly used in the plastics industry. On occasion however, metal powders like zinc might be used.

Plastics can also be reinforced. Fibrous materials are typically used to enhance both the strength and elasticity of plastics. The fibers used tend to be glass, carbon, aramid or basalt.

4. Key figures

PlasticsEurope is a European trade association (<http://www.plasticseurope.org/>). A large amount of data on plastics production worldwide, and more specifically in Europe, is available in their annual reports. Presented herein is a summary of the key figures drawn from their 2015 report (PlasticsEurope, 2015). Generally speaking, published data on plastics production rarely includes the fibers, namely PET, PA, PP and polyacryl fibers. Such is also the case for the PlasticsEurope data presented below.

4% to 6% of the world's oil production is used to manufacture plastics. In 2014, the global consumption level reached 311 million metric tons. Plastics production has increased exponentially, by nearly 100 million metric tons, in just 10 years. This increase corresponds to a 47% increase, over a period during which the world population only increased by about 12%. This evolution is mainly due to heightened production in Asia, and China in particular. In examining European data alone, plastics production has remained stable over the last 10 years (56 vs. 65 million metric tons). These figures do not indicate stability in European demand or consumption (Figure 5).

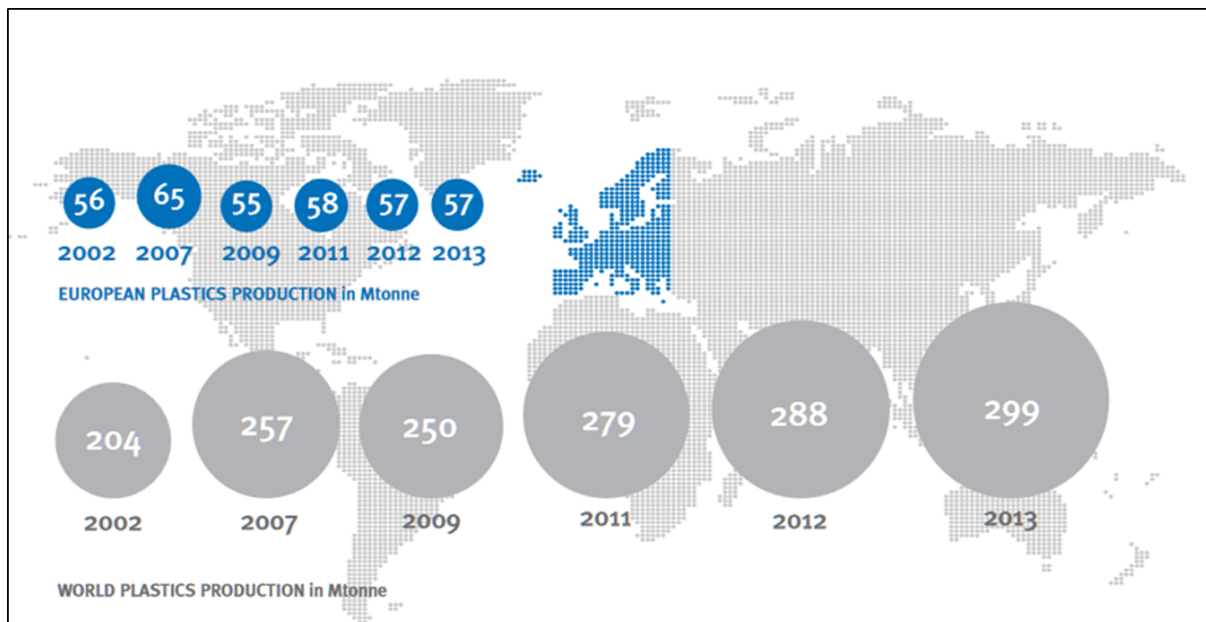


Figure 5: World and European plastics production between 2002 and 2013 (PlasticsEurope, 2015).

In Europe, the six polymers corresponding to the first six RICs are noteworthy for their market share, as they account for nearly 75% of all plastics demand in Europe. PE (including both high

and low density) is the most widely used polymer, representing 29.3% of total European demand. PP and PVC rank second and third in terms of demand, with market shares of 19.2% and 10.3%, respectively. PS and PET each make up 7% of the European demand. The remaining 25% of demand mainly encompasses: polyurethane (PUR), polytetrafluoroethylene (PTFE), acrylonitrile butadiene styrene (ABS), and polycarbonate (PC).

The most predominant use of plastics in Europe is for packaging, with a share of 39.5%, mainly accounted for by PE and PP (Figure 6). A 20.1% proportion of plastics, primarily PVC, is used in the building and construction sectors. The transport sector, coupled with the electrical and electronic segments, represent respectively 8.6% and 5.7% of European plastics uses. Other less predominant uses are found in various sectors, including agriculture, consumer and household appliances, furnishings, sports, and health and safety.

The fact that packaging constitutes the primary use of plastics underscores the pervasive nature of plastic waste given that packaging is designed for immediate disposal. It has been estimated that nearly 1.3 billion metric tons of municipal solid waste are generated every year throughout the world, with plastic representing 10% of this mass (Hoornweg and Bhada-Tata, 2012).

Of the plastics consumed in Europe, 25.1 million metric tons wound up in the waste stream in 2011 (PlasticsEurope, 2011). The PlasticsEurope report indicates that 59% of these plastics were recovered in the form of either energy reuse (34%) or recycling (25%). The remaining portion theoretically ends up in landfills but might have also leaked into the environment.

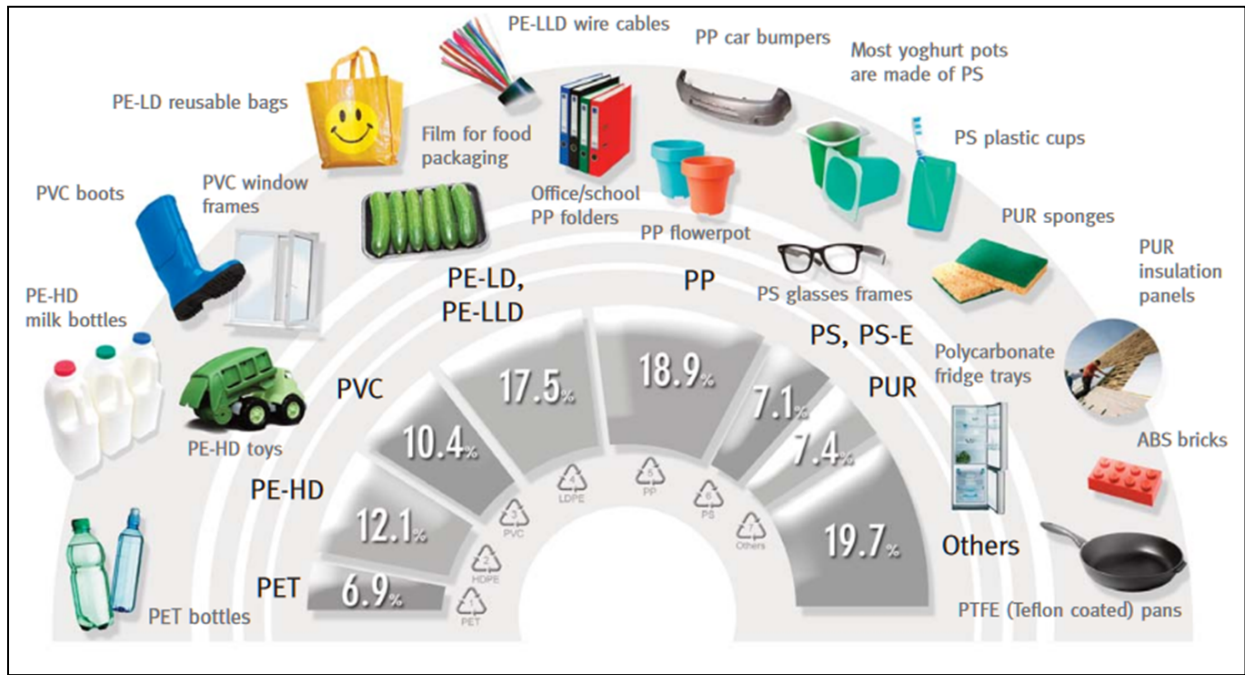


Figure 6: European plastics demand by polymer type in 2014 (PlasticsEurope, 2015).

5. Focus on fibers

As stated above, petrochemical fibers are not often included in the key figures published concerning plastic materials, yet a large proportion of the fibers produced do contain petrochemical polymers like PA. Some polymers indicated with one of the six specific RIC codes (e.g. PET, PP) can also have a fibrous form, thus excluding a proportion of production from the global figures. Fibers serve for many domestic uses, namely clothes, bed linens, curtains and carpets, chair coverings and upholstery, and ropes and fishing nets.

The International Organization for Standardization (in ISO/TR 11827:2012 Textiles - Composition testing - Identification of fibers) has proposed a classification of fibers by both their nature and origin (Figure 7).

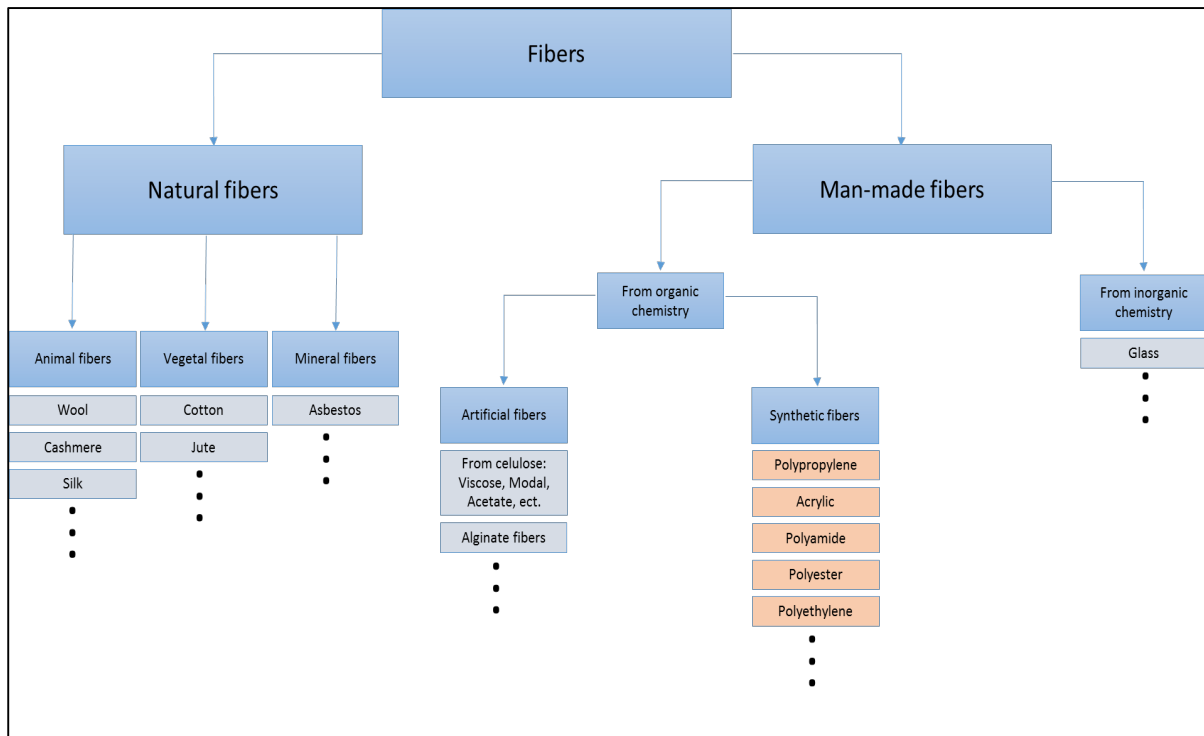


Figure 7: Classification of fibers used according to the International Organization for Standardization (ISO/TR 11827:2012 Textiles - Composition testing - Identification of fibers).

The fibers used can be either natural or man-made. Natural fibers are introduced just as they are found in nature; they are categorized according to their origin into animal, vegetal or mineral fibers. For instance, cotton is a very widely used natural vegetal fiber.

Man-made fibers are manufactured. Artificial fibers are produced by transforming natural polymers. As an example, rayon is artificially manufactured but still made from cellulose,

which is a natural vegetal polymer. Rayon is a generic term that encompasses all fibers derived from cellulose after several chemical processes. Specific types of rayon include viscose, modal and lyocell.

In contrast, synthetic fibers are made from chemically synthesized polymers. Plastic polymer (PP, PA, PES, etc.) fibers belong to this category. Bicomponent plastic fibers exist, with the two component fibers differing in their chemical or physical characteristics. PES is often used in copolymers with PA, PP or PE. Fibers made with both natural and synthetic polymers also merit mention.

Man-made fibers are manufactured industrially for various purposes; examples include: polypropylene fibers for upholstery textiles, acrylic fibers in cigarette filters, and artificial wool for sweaters. Nylon (PA) fibers are essential to the hosiery industry and in carpet manufacturing. Teflon is a chemical fiber used as a sealant for pipe threads and vessels; it can also be found in self-lubricating bearings.

The textile and apparel manufacturing industry relies heavily on man-made fibers. Cellulosic fibers and cotton blend fibers are widely used in clothing production. While cotton fibers are natural, textile manufacturing mixes cotton fibers with other fibers in order to change the properties of clothing. Polyester fibers are often blended with cotton to improve crease resistance. On the other hand, cotton may also be associated with synthetic polymers, not by blending but simply interwoven fibers. Interwoven cotton with PA is the most frequent case.

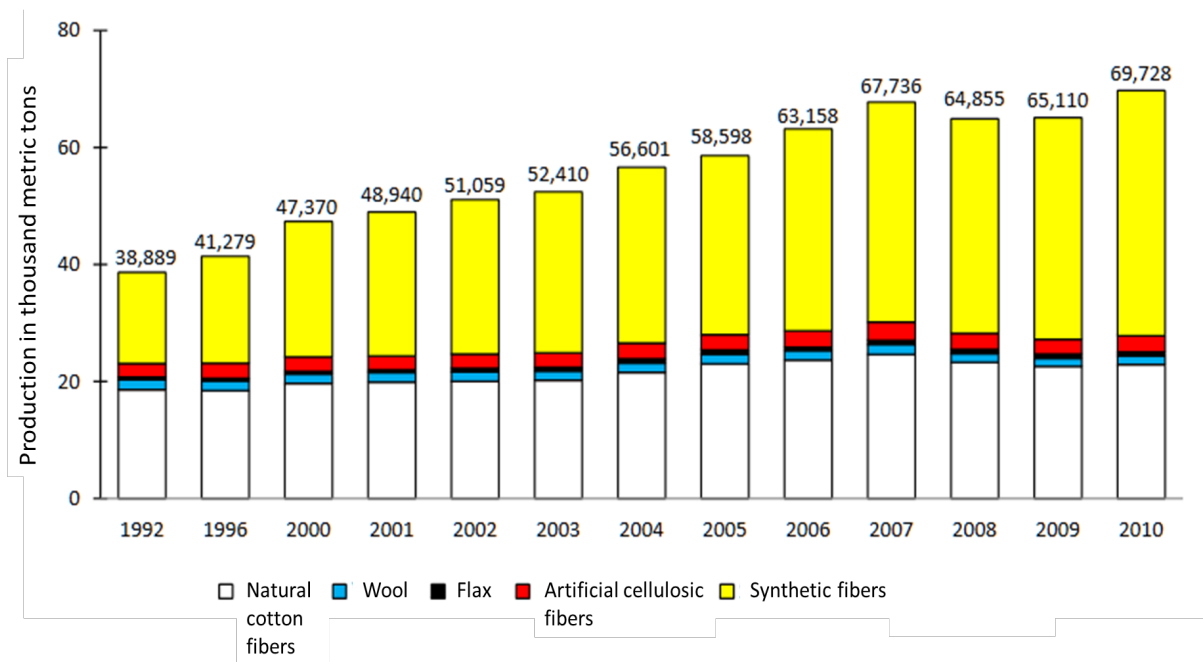


Figure 8: Production of natural and man-made fibers, 2000 - 2014 (000's of metric tons) (United Nations Food and Agriculture Organization, International Cotton Advisory Committee, 2013).

Natural cotton fibers accounted for 33% of fiber production in 2010, while artificial cellulosic fibers like rayon made up only 4%. Synthetic fibers were predominant with 60% of global production (Figure 8). The global production of man-made fibers has seen considerable growth since 2000 (Industrievereinigung Chemiefaser, 2015). In 2000, 31 million metric tons were produced. By 2011, this figure had risen to 52.7 million, of which 47.96 million were synthetic fibers and 4.74 million in artificial cellulosic fibers. In 2014, total fiber production reached 91 million metric tons, of which 63 million were man-made. The fraction of synthetic fibers is not insignificant and must be appended to the PlasticsEurope statistics presented in the previous section to obtain a global view of plastics production (Industrievereinigung Chemiefaser, 2015). Excluding synthetic fibers actually causes a 20% underestimation of plastics production.

II. Plastic pollution: From the macroscopic to the microscopic scale

The life of a plastic object is assumed to be a closed cycle thanks to recycling or a linear path from production to landfill or to elimination processes like incineration. However, despite existing waste management systems, plastic debris can be observed in environments across the whole world, whether marine or continental, thus revealing the presence of various leaks during the life cycle of plastic materials. While the issue of plastic pollution arose to address aesthetic concerns, its implications now extend to potentially harmful ecological or toxicological effects.

Plastics in the environment display a continuous spectrum of sizes, from very small particles to larger debris. The presence in marine environments of very small plastic debris, down to the millimetric scale, was first highlighted in the early 1970's (Carpenter and Smith, 1972; Carpenter *et al.*, 1972). It would take 30 years, in 2004, for the term "microplastics" to first be used to describe millimetric and inframillimetric particles, yet without providing a precise size definition (Thompson *et al.*, 2004). It must also be underscored herein that the prefix "micro" is associated with the Ancient Greek meaning of "*μικρός*: *small*" and not with the meaning of the metric scale prefix. As a matter of fact, microplastics do not necessarily lie on the micrometric scale.

For several years, the size of microplastics had remained poorly defined, and studies used different definitions. The upper limit of the microplastics designation was usually clearly stated in articles, while the lower limit went undefined and dependent mainly on the methodology employed (net mesh size, filter porosity, observation or analysis limit, etc.). In 2008, it was proposed to define plastic particles smaller than 5 mm as microplastics (Arthur *et al.*, 2008). This choice of a maximum was justified by a desire of the scientific community to focus the microplastics discussion on possible ecological effects other than physical blockage of gastrointestinal tracts. While no further explanation was given, this definition has been widely adopted by the studies published since. The present research program has also made use of this definition and strongly advises all future works to continue its application. While the word microplastics is not entirely satisfactory and even though the upper limit of 5 mm seems arbitrary, it is critical to respect this definition in order to avoid excessive heterogeneity

among studies and improve the ability to compare results worldwide. In contrast, particles larger than 5 mm are defined as macroplastics.

Table 1 illustrates how plastic particles have been defined in various environmental studies, by highlighting the evolution in the use of this word “microplastic” and its definition. Studies specifically targeting pellets were discarded since the microplastic definition used in these studies is inherent to the pellet shape and size. To provide a comprehensive view, the table also includes studies partially focusing on particles larger than 5 mm, despite their categorization as macroplastics. The table exposes the fact that microplastics are also often defined as plastic particles smaller than 1 mm.

Some studies refer to nanoplastics as even smaller particles. Until now however, no clear and unanimous definition has yet to surface and moreover very few environmental studies actually deal with this issue. In this context, very little scientific evidence is available regarding nanoplastics and, as such, it was decided to not discuss this subject herein.

Table 1: Reference studies focusing on microplastics, along with the definition provided for these particles.

| Reference | Year | Use of the word "microplastic" | Lower limit | Upper limit |
|---|------|-----------------------------------|-------------------|-------------|
| (Thompson et al., 2004) | 2004 | X | 1.6 μm | - |
| (McDermid and McMullen, 2004) | 2004 | | 1 mm | 15 mm |
| (Ng and Obbard, 2006) | 2006 | X | 1.6 μm | - |
| (Yamashita and Tanimura, 2007) | 2007 | | 1 mm | - |
| (Costa <i>et al.</i> , 2010) | 2010 | X | - | 1 mm |
| (Frias <i>et al.</i> , 2010) | 2010 | X | - | 5 mm |
| (Moore <i>et al.</i> , 2011) | 2011 | | - | 5 mm |
| (Martins and Sobral, 2011) | 2011 | X | 50 μm | 5 mm |
| (Claessens <i>et al.</i> , 2011) | 2011 | X | - | 1 mm |
| (Browne <i>et al.</i> , 2011) | 2011 | X | - | 1 mm |
| (Faure <i>et al.</i> , 2012) | 2012 | X | - | 5 mm |
| (Lusher <i>et al.</i> , 2013) | 2013 | X | - | 5 mm |
| (Van Cauwenberghe <i>et al.</i> , 2013) | 2013 | X | - | 1 mm |
| (Eriksen <i>et al.</i> , 2013a) | 2013 | X | - | - |
| (Mani <i>et al.</i> , 2015) | 2015 | X | - | 2 mm |

1. *Macroplastics*

1.1 *Macroplastics in marine environments*

Macroplastic debris is observed from boats everywhere on the planet (Barnes *et al.*, 2009). Mainly through indiscriminate dumping and accidental releases, plastics have been accumulating in the oceans over the years. During the 1980's and 1990's, plastic debris was found worldwide in various marine environments, including floating plastics in oceans and seas (Day and Shaw, 1987; Lecke-Mitchell and Mullin, 1992), as well as litter along coastlines and beaches (Pruter, 1987). From very early on, the increasing trend of marine litter has been observed, over just a 10-year time frame (Ryan and Moloney, 1993). This accumulation trend however was highlighted simply by the amount of litter stranded on the west side of an island. This local accumulation does not justify extrapolation to a global volume, especially knowing that plastic debris sinks and pathways in the oceans still require further investigation.

Subsequently, Charles Moore discovered the Great Pacific Garbage Patch. Due to the ocean currents, plastic debris tends to accumulate after being trapped in the ocean gyres, leading to the formation of zones like the one found by Mr. Moore, with highly-concentrated floating plastic debris (Matsumura and Nasu, 1997). The mainstream media calls these zones of accumulation the "Great garbage patches". The scientific literature has emphasized these zones over the ensuing years. Both field studies and satellite observations have been conducted. For instance, one study used satellite observations to determine the surface circulation in the South Pacific Ocean, showing an accumulation of debris in the eastern-central region of the South Pacific Subtropical Gyre (Martinez *et al.*, 2009). A field study in the North Pacific Central Gyre estimated that the mass of plastics ($5,114 \text{ g.km}^{-2}$) in 2011 equaled approximately six times the mass of plankton (Moore *et al.*, 2001). Garbage accumulation zones were also detected in the North Pacific Subtropical Gyre (Titmus and Hyrenbach, 2011), as well as in the South Atlantic (Ryan, 2014). Until very recently, the common belief was that once in an accumulation zone, plastics would converge at the center and remain trapped. Small escape routes have however been exposed more recently (Maes *et al.*, 2016). This team used a fine-resolution model (3 km vs. the 50-100 km resolution used in oceanographic or climatic studies) in order to estimate the plastic debris outflow that can be trapped in the Pacific Gyres. The authors have hypothesized that plastics escaping from the gyres might even

return to the coasts. This updated knowledge is of tremendous interest and serves as additional proof of the current lack of understanding of plastic pollution dynamics.

Given that these accumulation zones have drawn the attention of the scientific community for years, they have attracted a much larger share of oceanic expeditions, thus leading to sparser coverage elsewhere, even though plastics are not restricted to the oceanic gyres and do present a global challenge. Macroplastics have been observed worldwide, even far from anthropized areas, e.g. in Antarctica (Barnes *et al.*, 2010). The distribution and abundance of large marine debris have been investigated in the European seas, including the Baltic Sea, the North Sea, the Celtic Sea, the Bay of Biscay and the Mediterranean Sea. This study has revealed the influence of geomorphological factors, local anthropogenic activities and river inputs. Accumulation zones could also be detected in the southern part of the Celtic Sea and along southeastern France (Galgani *et al.*, 2000).

In this context and knowing that plastic pollution is ubiquitous within the marine environment, a primary goal of this work program is to estimate the global abundance and weight of floating plastics. While many studies over the years have focused on describing local contaminations, estimations of the quantities of plastics in the marine environments still lack precision. This shortcoming appears to be a real challenge since such expeditions are expensive and the ocean is vast and ever-changing, with plastic pollution exhibiting high spatial and temporal variability (Howell *et al.*, 2012). A study based on surface net tows (N = 680) and visual survey transects of large plastic debris (N = 891) across various places, coupled with an oceanographic model of floating debris, estimated that a minimum of 5.25 trillion particles, weighing 268,940 tons, were present in the world's oceans (Eriksen *et al.*, 2014).

This estimation was based on surface trawls. Studies almost exclusively focused on the ocean surface. Much plastic debris is in fact due to its buoyant density in ocean waters; some polymers however have a higher density, and the lighter ones are buoyant until they become waterlogged or accumulate too much biota. The ocean floor has clearly not been studied adequately. A recent published work, based on the Mediterranean International Bottom Trawl Surveys (MEDITS) carried out in the Mediterranean and Black Seas, stated as a rough estimation that between 71.5 and 116 billion large pieces of plastic debris are present on the sea floor, without accounting for microplastics, which might even be more numerous (Galgani,

2015). This finding would suggest that the deep-sea floor is probably a final global sink for marine litter and moreover that the proportion of plastics investigated until now is just the tip of the iceberg. We are not in possession of any inventories of significant debris accumulation in deep and remote areas and know very little about deep-sea currents and likely deep convergence zones. It is highly plausible that many deep-sea accumulation zones have yet to be discovered.

The consequences of macroplastic pollution, beyond the aesthetic nuisance and impacts of limiting tourist activities and increasing beach clean-up costs, may be considerable. Warnings have been issued for a long time that plastic litter could injure or kill a wide range of animals that get entangled in or eat it, along with the potential to disperse terrestrial organisms (Shomura and Godfrey, 1990). The entanglement of marine species, like mammals, turtles and sea birds, has been fully described (Barnes *et al.*, 2010; Carr, 1987; Rochman and Browne, 2013). It was estimated that worldwide more than 100,000 sea animals die from eating or being caught in plastic bags and other plastic debris (Wilks, 2006). This estimation was published in 2006 and is therefore somewhat outdated. While the effects of macroplastics are often described (mainly using examples of entangled animals or ingested litter), the scientific community's interest has shifted over the last decade: recent findings and works focus nearly exclusively on the impact of microplastics (see Section II-2.2 of this chapter). For macroplastics, despite considerable attention paid to ingestion, the real impact is still poorly understood. A study on a Portuguese coast showed that though 59% of the 95 investigated dead turtles had ingested litter, it was impossible to conclude any correlation in the cause of death and size of turtle with the amount of litter ingested (Nicolau *et al.*, 2016).

1.2 Macroplastics in continental areas

While the extensive fishing and maritime and recreational uses of oceans represent an obvious source of plastic debris in the marine environment, it is widely cited that 80% of this debris stems from the continental environment (Andrady, 2011; Cole *et al.*, 2011; Jambeck *et al.*, 2015; UNEP, 2009). Until now however, only limited data have backed this estimation as more knowledge is needed. One major issue relative to macroplastics in continental areas is to produce an accurate estimation of the mass of plastics flowing from rivers into oceans and then assess the extent of the continental zone as a source. Compared to the tremendous

amount of data available on macroplastics in marine environments, very few studies have been conducted in freshwater media.

Using a simple statistical modeling approach, a study has approximated the mass of continental plastics entering the marine environment (Jambeck *et al.*, 2015). This estimation was based on worldwide data compiled on solid waste, population density and economic conditions; it focused on information regarding 192 coastal countries since they are considered the greatest contributors to ocean contamination. It has been estimated that between 4.8 and 12.7 million metric tons of plastic entered the ocean in 2010. In comparing these very high estimates with those of plastics present in the world's oceans, as described above (i.e. 268,940 tons), a large discrepancy becomes apparent between the annual continental flux and the oceanic stockpile, implying major gaps in knowledge when assessing the dynamics of plastics in oceans. This huge difference could, for instance, be partially ascribed to the fact that the estimations by Eriksen *et al.* (2014) were based on plastics floating on the ocean surface, whereas the supposition could be made that a significant share of the macroplastics will sink and accumulate on the seabed. Moreover, a rather large proportion of Jambeck's estimation might never actually reach the oceans and instead be deposited directly along the shore. These estimations require greater refinement: they have relied heavily on a percentage of mismanaged plastic waste that has been only very roughly determined and remains difficult to estimate accurately.

Field investigations for macroplastics in continental areas are needed to corroborate the initial estimates proposed by Jambeck, yet such investigations remain quite rare. A study was conducted in the Thames River (Morritt *et al.*, 2014), where eel nets were attached to the riverbed, allowing all waste to be collected within 40 cm above the riverbed. The collected objects were then visually sorted and counted. The authors found 8,490 plastic items over a three-month period. No characterization was performed, though this article will provide information on submerged plastics, as opposed to the general tendency to focus exclusively on floating debris, thereby underestimating plastics flows from rivers into the oceans.

Another study investigated riverbank abundance and composition of macroplastics [> 1.5 cm] from four rivers flowing into the Southeast Pacific, starting at the headwaters down to the river mouth (Rech *et al.*, 2014). Plastics were the prevailing litter items at most sampling sites,

with their number ranging from 15% to 73% of total collected items. The total abundance of plastics remained below 4 items.m⁻². No specific pattern was observed along the river from headwaters to river mouth. Hence, hydrology did not seem to be a key factor determining plastic abundance; their variability was more closely correlated with land use and river shore accessibility, both capable of facilitating activities like illegal waste dumping.

Due to the lack of studies on macroplastics in continental environments, let's also examine clean-up operations for additional data. Our interest here focuses more specifically on the efforts conducted by the non-governmental organization (NGO) "Mal de Seine" owing to the proximity of the study site selected for this thesis. The goal of this clean-up operation was to assess the annual quantity of debris ending up on the Seine riverbank, close to its estuary. For this purpose, 100 meters of riverbank are cleaned once a year, in counting the number of collected items. Between the 2012 and 2013 campaigns, a total of 5,274 plastic objects accumulated within the study area, thus making it possible to monitor the temporal evolution of waste traveling towards the sea. These items were visually identified while not proceeding with an actual characterization of the plastic items collected during clean-up. The identification of plastics can be considered as correct given that the type of large-sized debris is usually easily recognized. The classification ascribed however is not always accurate since some items may straddle two or more categories. For example, items in the category "plastic pieces" might also be classified "other plastic items", without any distinction being made between the two "candy" categories. This campaign therefore does not yield precise information on macroplastic fluxes, although the method employed allows assessing the contamination of continental areas by macroplastics. Moreover, even if we could observe the fraction not reaching the ocean, the macroplastics deposited on riverbanks could, when not discarded, be transported during flood events into marine environments.

The present synthesis reveals that macroplastics in the continental environment have received far too little attention, most certainly the result of a combination of aspects. First of all, the continental environment has not benefited from the presence of spectacular accumulation zones, like the oceanic garbage patches, in order to generate media interest. Next, when rivers started to be considered as potential major sources of plastic pollution in 2009 (UNEP, 2009), the scientific community was focusing on the more attractive topic of

microplastics. One proof that macroplastics were being considered as a public concern but of no scientific interest lies in the fact that a specific methodology was never employed by different teams to allow for comparisons between rivers. All the surveys presented above actually used different methods, i.e. from eel nets installed at the bottom of the Thames all the way to a theoretical global approach. This point also sharply contrasts with the fact that continental investigations would be less expensive to conduct than their marine counterparts.

The main consequence here is the lack of information on the amount of plastic flowing into oceans from rivers. Eriksen *et al.* (2014) showed that microplastics, while present in greater quantities, only accounted for 10% of the global plastic waste. Neglecting the macroplastics in rivers could thus lead to overlooking the larger proportion of plastic mass inputs.

2. General information on microplastics

2.1 Microplastic types

Microplastics cover a broad and continuous spectrum of sizes and shapes, including fibers and lines, films, fragments, spheres (Figure 9). Depending on their origin, microplastics can be either primary or secondary materials.

Primary microplastics are already being manufactured at the millimetric or submillimetric scale. Two forms of primary microplastics can be distinguished: preproduction pellets, and microbeads. Preproduction pellets are used in the plastics industry. These virgin resins are melted and then formed into consumer products (Wilber, 1987). They are rounded and typically have a diameter between 2 and 5 mm (Costa *et al.*, 2010). They have sometimes been referred to as mesoplastics (Gregory and Andrady, 2003). Even though their size lies in the range of the microplastic definition, some authors have questioned whether they should be included in the microplastic category or be considered separate (Andrady, 2011; Cole *et al.*, 2011; Costa *et al.*, 2010), due to the fact that all resin pellets are visible to the naked eye and can be handled.

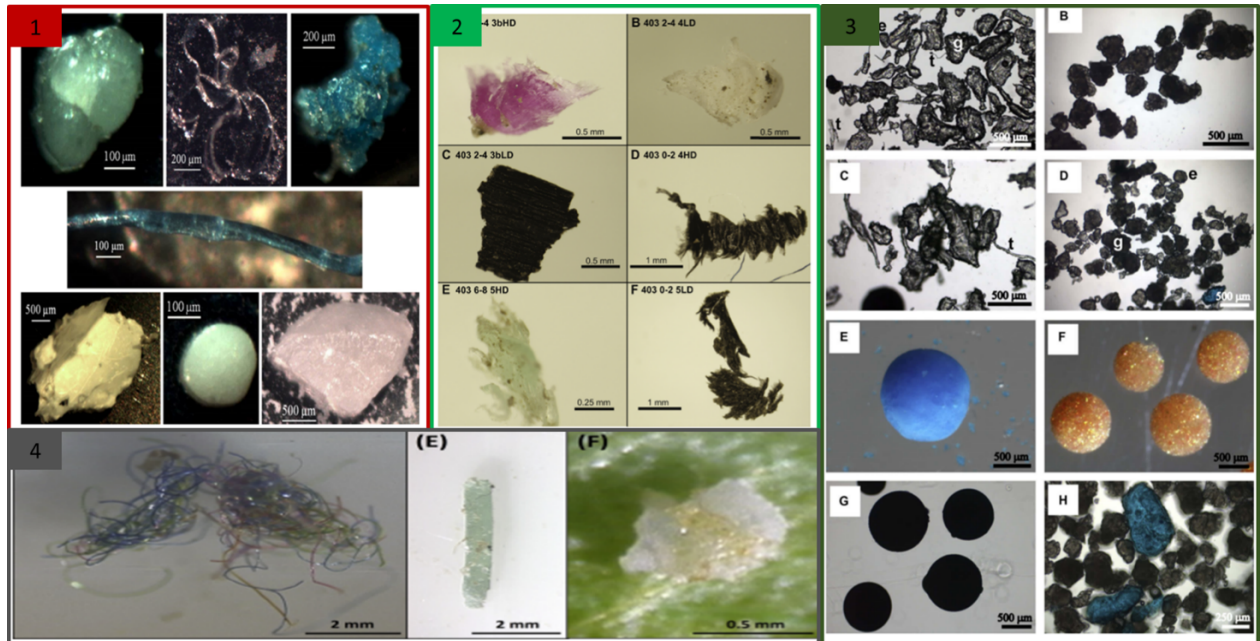


Figure 9: Microplastics of various shapes: 1) Microplastics isolated from fish stomach content including fragments, fibers and spheres (Collard et al., 2015); 2) Plastic fragments collected from bottom sediment in Lake Ontario (Corcoran et al., 2015); 3) Microplastics detected in various facial cleansers (Fendall and Sewell, 2009); 4) A fiber, a line and a pellet (from left to right) found in manta trawl samples in Lake Hosgovol (Free et al., 2014).

Primary microplastics, typically called microbeads by the industry, were considered by some authors in the 1990's as an additional albeit minor source of plastic pollution. These primary microplastics in fact were first introduced into hand cleansers only used on rare occasion by the average consumer (Gregory, 1996). Since that time, microplastics have replaced natural exfoliating agents in facial cleansers, which are often used on a daily, or at least weekly, basis. A study was conducted on four facial cleansers commercialized in New Zealand (Fendall and Sewell, 2009); it showed that the median size of these PE particles, depending on the product, varied between 190 and 375 μm . This study also indicated that microplastic fragments contained in the facial cleansers have various 3D shapes, including spheres, granular particles, ellipses, threads and irregular particles. The authors pointed out the fact that these microplastic particles could enter aquatic environments through wastewater. A more recent study found a similar size distribution, between 164 and 327 μm , in facial scrubs (Napper *et al.*, 2015); it also estimated that between 4,594 and 94,500 microbeads could be released in just a single use. While studies have focused on PE microbeads present in facial scrubs, microbead uses are actually far more varied in cosmetics, e.g. in soaps, toothpaste, shaving

foam, bubble bath, sunscreen and shampoo. Moreover, given that some 93% of products use PE, microbeads can also be composed of PP, PET or PA (UNEP, 2015).

No precise information has yet to appear in the literature on the extent of microbead contribution to microplastic pollution. The amount discharged into wastewater could be easily calculated by knowing the sale volume of each product and then multiplying these data by the microplastic ingredient content. Unfortunately, this information is not publicly available. It has however been published in a Norwegian report, estimated from a personal memorandum from PlasticsEurope, according to which 4,000 metric tons of microbeads are used annually in Europe, i.e. equivalent to 8 grams per capita per year (Norwegian Environment Agency, 2014). An alternative approach was conducted by estimating the amounts released into freshwater ecosystems, in relying on a consumer survey (178 participants) to determine how often and how much microbead product is being used. After applying the effect of WWTP (wastewater treatment plant) microbead removal efficiency (70%), it was estimated that over 800 metric tons are being released in the European Union each year (Kalcikova and Zgajnar, 2016). By applying the same WWTP removal rate to the Norwegian report estimations, both studies provide consistent results.

Microbeads have received a considerable amount of media attention. As a result of increased overall awareness of the problem, many companies that use microbeads in their products have been phasing them out voluntarily, especially in recognition of the fact that the industry believes microbeads can and will be easily replaced by better natural alternatives. The “beat the microbead” plastics program, supported by 79 NGOs across 35 countries has succeeded in convincing 337 brands to remove plastic microbeads from their products (<https://www.beatthemicrobead.org/en/results>). The Microbead-free Waters Act was signed in December 2015 to ban the production and importation of cosmetic products containing microbeads in the U.S. The Australian government initiated a voluntary phase-out of microbeads, which if not proven efficient by 1st July 2017 will lead to enactment of a legal ban. In the European Union, a similar plan of voluntary removal of microbeads was launched. The German and Dutch parliaments were the first to take major steps towards banning microbeads.

In light of all these worldwide efforts, it is apparent that in the near future microbeads will be completely phased out of consumer products, thus mitigating the threat from primary microplastics. On the other hand, the issue of secondary microplastics remains a major one.

Secondary microplastics stem from the degradation and fragmentation of large debris in the environment. The types and shapes of microplastics found in various studies show that these fragments originate from the breakdown of a wide range of everyday plastic products (Barnes *et al.*, 2009). The various factors involved in the fragmentation process comprise thermal, mechanical, biological, physical and photo-degradation (Cooper and Corcoran, 2010; Gregory and Andrady, 2003). Once weakened by UV radiation, weathering and thermal impacts, the material undergoes physical fragmentation due to waves, wind or fouling (Galgani, 2015). Biological degradation also plays a role in the fragmentation process. The primary mechanism in the biodegradation of synthetic plastic polymers is oxidation or hydrolysis by enzymes, in creating functional groups to improve its hydrophilicity (Shah *et al.*, 2008). When located inland or deposited on beaches, the debris will fragment more rapidly than in the open ocean or in freshwater due to a higher exposure to UV radiation and wind-induced physical processes (Biesinger *et al.*, 2011; Corcoran *et al.*, 2009). The topic of degradation kinetics requires further investigation, given its relationship to polymers, chemical additives and environmental factors. This knowledge is crucial to determining the quantity of microplastics expected to form from macroplastic pollution and at which time scale. Continuous fragmentation is also key to predicting the life cycle of microplastics in the environment before they decrease in size. For instance, a recent study has hypothesized the existence of a discontinuity in the fragmentation process (ter Halle *et al.*, 2016). The smaller microplastics (i.e. below 2 mm) fragment much faster due to the apparent rolling at sea, hence leading to less colonization. The larger ones (2 to 5 mm) are generally flatter with one surface more heavily photo-degraded while the other surface (i.e. the immersed one) containing more biofilm. The fact of floating in a preferred direction slows their degradation.

While degradation is occurring on the surface water and beaches, it seems to be very slow for settled plastics. A study has pointed to PE plastic bags as well as to bioplastics in temperate marine sediments (Nauendorf *et al.*, 2016). For both materials, despite the high bacterial colonization, no signs of degradation appeared after 98 days, hence also displaying the

potential of marine sediments as a long-term sink for plastic litter, even for supposedly compostable material.

While primary and secondary microplastics are generally easily distinguished, textile fibers present a special case. They may be considered as secondary microplastics since they originate from the breakdown of larger items (clothes). Unlike previous cases, this breakdown does not occur in the environment, but rather inside washing machines when doing laundry (Browne *et al.*, 2011). Consequently, fibers are found in washing machine effluent and, like primary microplastics, enter the environment at a microscopic size.

2.2 Impact of microplastics

Microplastics contained in hydrosystems may either physically interact with the biota or chemically interact by exchanging chemicals with their environment.

a. Interaction with the biota

The initial proof of plastics in the environment began with a study on biota. In the late 1960's, an examination of the gut contents of seagulls demonstrated that they were ingesting plastic material (Kenyon and Kridler, 1969). Since plastics are present in the environment across a continuous spectrum of sizes, from large debris to very small microplastics, an extremely wide range of organisms are able to ingest them.

Microplastic ingestion has been widely reported in the environment by various organisms, mainly marine, throughout the food chain. Lower trophic-level marine organisms also ingest microplastics. The ingestion of plastics was very quickly and early identified in at least 267 marine species (turtles, seagulls, marine mammals, etc.) (Laist, 1997). This figure is probably outdated. It has since been shown that this ingestion phenomenon is widespread. Plastics were found in the gut of common planktivorous fish in the North Pacific Central Gyres (Boerger *et al.*, 2010). Several deep-water fish species ingested plastic bag fragments, fishing gear fragments and textile fibers (Anastasopoulou *et al.*, 2013). In the English Channel, five pelagic and five demersal species ingested microplastics, mainly fibers. Rayon, considered by the authors of this study as a microplastic, and PA have been the predominantly ingested polymers (Lusher *et al.*, 2013). Generally speaking, ingestion has been demonstrated for many

marine organisms, including lugworms, barnacles, amphipods (Thompson *et al.*, 2004) and crustaceans (Murray and Cowie, 2011). Most often, the organisms may voluntarily ingest the microplastics, in confusing them for prey (Cole *et al.*, 2011).

While ingestion is now an attested phenomenon for many species, the impact of this ingestion as well as the possible translocation and trophic transfer of the ingested plastics remain open to question. The term translocation in this context means that the microplastics are not excreted or retained in the digestive system but instead incorporated into the body tissues and fluids of the organism (Wright *et al.*, 2013). If translocation were confirmed, this would also mean that microplastic ingestion could result from trophic transfer, with organisms eating lower trophic organisms that themselves had consumed microplastics. Some studies have attempted to prove translocation in laboratory experiments. One laboratory study found that crabs (*Carcinus maenas*) may have microplastics in their tissues after eating mussels (*Mytilus edulis*) exposed to microplastics. This study seems to provide evidence of trophic transfer as well as microplastic translocation (Farrell and Nelson, 2013). A translocation experiment was performed with mussels (*Mytilus edulis*) exposed to 3 and 9.6 μm particles. After 3 days, translocation to the circulatory system was observed and consisted of a greater number of smaller particles compared to the larger microplastics (Browne *et al.*, 2008). In agreement with these findings, another study detected microplastic occurrence in the soft tissues of cultured *Mytilus edulis* and *Crassostrea gigas* (Van Cauwenberghe and Janssen, 2014). These studies show that microplastics can be translocated into tissues, but further studies are still needed to address this aspect more fully and with more evidence. The natural process of digestion is supposed to prevent larger particles, like those observed in the previous studies, from passing into the internal body. This body protection function was corroborated for sand particles, which were excreted and not translocated (Hussain *et al.*, 2001), and should work similarly for microplastics. A recent work has revealed that shrimp in the Channel area and southern part of the North Sea ingest synthetic fibers, yet the authors also indicated that such fibers were not capable of translocating into the tissues (Devriese *et al.*, 2015).

While translocation has become more readily refuted, this does not suggest that ingesting microplastics exerts no impact. The effects induced by these particles however are still poorly documented, and major questions need to be investigated further. Once ingested,

microplastics could block the passage of food through the intestinal tract (Tourinho *et al.*, 2010). A reduced food intake could also be caused by the microplastics, which yields a false indication of satiation to the organisms (Derraik, 2002). Particles have also been proven to interact with mammalian cells in the intestinal system (Carr *et al.*, 2012).

Some recent laboratory studies have exposed potential effects. One study showed that zooplankton, an organism with a vital ecological role in food webs, is capable of ingesting microplastics (Cole *et al.*, 2013); this ingestion has a negative effect on zooplankton by virtue of significantly decreasing its algal feeding and adversely impacting its growth. In another study, it was demonstrated that water spiked with PS nanoparticles altered algal photosynthesis (Bhattacharya *et al.*, 2010). Marine lugworms exposed to sediments spiked with PS suffered from reduced feeding and weight loss (Besseling *et al.*, 2013).

As opposed to the previous observations, a number of studies did not observe any significant effects from microplastics. The exposure of sea urchin larvae *Tripneustes gratilla* to PE microspheres showed a very small, and insignificant, effect on the survival of these organisms, even though the concentration used exceeded those recorded in the marine environment. Similarly, PET microplastics, after a 48-day exposure on juvenile and adult *Gammarus pulex* individuals, did not reveal any long-term effects (Weber *et al.*, 2016). In both these studies, ingestion was actually observed.

Further work is still required to gather knowledge on the impact of microplastics, including their effect on growth, reproduction and mortality. In general, laboratory experiments focusing on this issue use very high concentrations outside the range of environmental relevance. More realistic studies are still needed to develop a more accurate opinion of the risks involved. Moreover, the particles used in these tests are often spherical, and PS is the most heavily tested polymer. The effect of other polymer shapes (i.e. mainly fibers, which are predominant in the environment) have not been properly studied. Exposure studies typically involve specific polymers with specific shapes and a single precise size, while *in situ* exposure is much more diverse, with a large array of polymers, sizes and shapes. Also, in the environment, plastics are associated with chemicals and biofilms, which is not the case in the majority of laboratory experiments involving virgin plastics.

Another type of interaction between biota and plastic particles is the colonization of these particles by marine organisms. The presence of plastic debris recalls that the colonization by alien species poses one of the greatest threats to world biodiversity. After investigating marine organism colonization of drift debris deposited on the shores of 30 remote islands across all oceans from Arctic to Antarctic, it was shown that plastic litter more than doubles the rafting opportunities for biota, particularly at higher latitudes (Barnes, 2002). It can thus be assumed that microplastics also serve to support the biota. For instance, plastic debris might serve as a vector for dispersing harmful algal bloom species (Maso *et al.*, 2003). More recently, the microorganisms associated with microplastics have been investigated. PE, PP and PS particles collected from the North and Baltic Seas proved the presence of *Vibrio spp.*, which are potentially pathogenic species (Kirstein *et al.*, 2016). The colonized particles could therefore function to disperse pathogens into the marine environment and introduce them into organisms. This risk remains quite uncertain and should be investigated in future work.

b. Pollutants and microplastics

It has been demonstrated that plastics are often associated with a "cocktail of chemicals" (Rochman and Browne, 2013). This association can either be correlated with the fact that such pollutants are adsorbed onto the plastic debris once in the environment or else be due to the fact of incorporating pollutants as additives during the plastics production process.

Trace metals were revealed to accumulate from seawater on plastic pellets (Ashton *et al.*, 2010) but were studied to a lesser extent than organic pollutants. Plastic pellets collected from the beaches of southwest England contain variable concentrations of trace metals (Cr, Co, Ni, Cu, Zn, Cd and Pb). These concentration levels sometimes exceeded those reported for local estuarine sediments (Holmes *et al.*, 2012). To the best of our knowledge, the adsorption of trace metals has only been studied in pellets.

Organic pollutants were slightly more extensively studied than trace metals. Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethanes (DDTs) were all found on pellets collected from Portuguese beaches (Frias *et al.*, 2010). PCBs on beach resin pellets can reach high levels, and it was suggested in a study that these pellets might be the predominant source of exposure to

contaminants at remote sites (Endo *et al.*, 2005). Remote islands in the Pacific, Atlantic and Indian Oceans have also yielded pellets with very high levels of adsorbed PCBs, DDTs and hexachlorocyclohexanes (HCHs) (Heskett *et al.*, 2012). The sorption of hydrophobic contaminants on plastics greatly exceeds their sorption on natural particles, while desorption occurs more rapidly from natural particles than from plastics (Teuten *et al.*, 2007). In addition to the adsorbed pollutants, additives such as bisphenol A, octylphenol and nonylphenol were detected in marine plastic fragments (Teuten *et al.*, 2009). Since additives have already been discussed in the first section of this thesis, they will not be presented herein.

While it is known that microplastics can act as passive samplers as regards various pollutants, their contribution to and effect on total pollution in the environment remain to this day unknown. We also lack the knowledge to determine whether microplastics will enhance the uptake of these pollutants by organisms and provide a significant contribution as a pathway compared to natural debris. It has been estimated that the addition of as little as 1 µg of contaminated PE per g of sediment increases phenanthrene accumulation by the lugworm (*Arenicola marina*) (Teuten *et al.*, 2007), thus indicating that plastic might be an important agent in the transport of hydrophobic contaminants to organisms. A PS dose of 0.074% in contaminated sediments increased PCB bioaccumulation by a factor of 1.1-3.6 for the lugworm (*Arenicola marina*) (Besseling *et al.*, 2013).

Further work is needed to estimate the environmental implications with continued uncertainty. Moreover, only studies on marine or estuarine (Bakir *et al.*, 2014) environments have been conducted. Freshwater systems display different conditions compared to marine systems (salinity, organic debris, hydrodynamic conditions, etc.), and POP concentrations in the continental environment are expected to exceed those in marine ecosystems. It is essential therefore to address interactions between micropollutants and plastics in freshwater, by specifically focusing on the urban lakes and rivers known to be more highly contaminated.

2.3 Microplastics in marine environments

a. Buoyant microplastics

Microplastics have been spotted in marine environments since the early 1970's. Due to the numerous published studies, especially during the last decade, on microplastics in marine water, this section is far from being exhaustive and merely seeks to offer a glance at the ubiquity of plastic contamination and highlight the disparity of investigation methods used.

An initial study reported densities of up to 10^5 synthetic fibers. m^{-3} in the North Sea (Buchanan, 1971), although these fibers might mainly be cellulosic. This work did not receive much attention. The concern only arose when the two traditionally cited papers published by Carpenter in 1972 revealed the presence of plastic particles in marine environments (Carpenter and Smith, 1972; Carpenter *et al.*, 1972). Small plastics were collected in the Sargasso Sea, containing an average of 3,500 particles. km^{-2} (Carpenter and Smith, 1972). Plastic particles, mainly identified as pellets, were first encountered accidentally when sampling microalgae with a 330 μm neuston net. Since then, many studies have been carried out in various marine environments, from the water surface using a similar sampling method (330 μm mesh size nets) to marine or beach sediments. Microplastics were detected in all oceans, but mainly in the Atlantic (Ivar do Sul *et al.*, 2014; Lusher *et al.*, 2014; Reisser *et al.*, 2015) and Pacific Oceans (Moore *et al.*, 2001; Yamashita and Tanimura, 2007). Microplastics have also been reported in the Mediterranean Sea (de Lucia *et al.*, 2014) and English Channel (Cole *et al.*, 2014), as well as in coastal waters like in Australia (Reisser *et al.*, 2013).

The various studies conducted worldwide across an array of environments have shown the presence of pellets, fibers and particles of different shapes and at very different concentrations. Depending on the study, the predominant type of plastics would be either fragments (Eriksen *et al.*, 2013b; Ivar do Sul *et al.*, 2014) or fibers (Desforages *et al.*, 2014; Lusher *et al.*, 2014). These differences become even more pronounced when including the temporal factor. A 2012 study found high levels of microplastics, reaching 350,000 particles. km^{-2} in the northwestern Mediterranean Sea (Collignon *et al.*, 2012). The huge difference between these results and those published in 1972 is also reflective of the improvement in methods being used in addition to an increase in microplastic contamination or a site effect. The 1972 study was based on a visual inspection of the samples, whereas the other approach, as is the case for many recent studies, used a stereomicroscope. The

underlying general methodologies have evolved from naked eye inspections to stereomicroscope observations and, ultimately, to chemical identification.

In general, the differences between studies could be both site and time-related but might also be primarily due to the very high heterogeneity existing among the methodologies employed. All steps actually vary from one study to the next, thus practically nullifying the possibility of drawing any comparisons (Table 2). This difficulty drawing comparisons is compounded by the units used. Concentrations are mainly expressed in two different units, i.e. the number of particles per surface area unit (items.m⁻² (Cózar *et al.*, 2015), pieces.km⁻² (Law *et al.*, 2010), etc.) and the number of particles per volume unit (fibers.L⁻¹ (Buchanan, 1971), particles.m⁻³ (de Lucia *et al.*, 2014), etc.).

Table 2: The various methods used at each step when analyzing microplastics. This table has been based on the review derived by Hidalgo-Ruz *et al.*, 2012 and is intended to be highly synthetic.

| Sampling | Bulk water |
|--------------------------|---|
| Sample processing | Net samples with a mesh size ranging from 53 to 3,000 µm |
| | Sieving before filtration with sieves sized for meshes between 38 and 4,750 µm |
| Identification | Direct filtration on filters, with a porosity varying from 1 to 2 µm |
| | Only visual sorting with the naked eye or stereomicroscope |
| | Chemical identification using FTIR or Raman spectroscopy |

b. Non-buoyant microplastics

For a long time, plastics were considered to be buoyant, and the focus of research efforts mainly pertained to the neustonic layer of marine water. Surface trawling is the commonly used sampling method. Some plastic polymers however have a density higher than that of marine water (Hidalgo-Ruz *et al.*, 2012). Also, the accumulation of microbial biofilms, the

colonization of algae and invertebrates on the plastics surface and the evolution in physicochemical characteristics of plastics in both freshwater and seawater all tend to increase particle density, in leading them to the sink (Andrady, 2011).

Biofouling, for example, can occur in seawater very rapidly. An experimental study has shown that in slightly less than one week, plastics submerged in Plymouth harbors (UK) presented a visible biofilm on their surface and became less buoyant over time (Lobelle and Cunliffe, 2011). By the end of this 3-week experimental period, the plastic had moved away from the surface and become neutrally buoyant, leading to the conclusion that water column and marine sediments also need to be investigated. According to this hypothesis, microplastics could even be found in deep-sea sediments, ranging in depth from 1,100 to 5,000 m (Van Cauwenberghe *et al.*, 2013).

A recent study conducted in the Arctic polar waters was among the first to propose a comprehensive approach, by sampling both surface (top 16 cm) and subsurface (6-meter depth) waters (Lusher *et al.*, 2015). The subsurface waters were sampled with a seawater pump, making it possible to sample 2,000 L over a 2-hour period. It was shown that 93% of the subsurface samples ($n = 75$) contained microplastics, with concentrations averaging $2.68 \text{ particles.m}^{-3}$, which was higher than the average surface concentrations ($0.34 \text{ particles.m}^{-3}$). Fibers accounted for 95% of all microplastics identified.

c. Microplastics in marine sediments

To date, marine sediments have been very poorly investigated.

Sediments near the Belgian coast exhibited concentrations reaching $390 \text{ particles.kg}^{-1}$, with fibers also being predominant (Claessens *et al.*, 2011). This predominance of fibers has often been noticed in both marine and estuarine environments ever since Thompson's 2004 paper (Hidalgo-Ruz *et al.*, 2012; Thompson *et al.*, 2004). Beach sediments have also been contaminated. As early as 1978, it was highlighted that small virgin plastic granules were abundant in 300 New Zealand beaches (Gregory, 1978). A study estimated that along the Portuguese coastline, 72% of plastic objects are smaller than 5 mm (Martins and Sobral, 2011). In beach transects on the Frisian Islands, particles in the shape of both granules and fibers have been detected while fragments were completely absent (Liebezeit and Dubaish, 2012).

In contrast, fragments were predominant (96.7%) on a Brazilian beach, yet the authors made no mention of any fiber (Spengler *et al.*, 2008).

As for the buoyant microplastics, various studies have applied quite different methods and have examined different plastic sizes and types (pellets, microbeads, fibers) of microplastics (Hidalgo-Ruz *et al.*, 2012). In studies on sediments, various units have also been used, with the number of microplastic objects per surface area (Ismail *et al.*, 2009), per mass of sediment (Liebezeit and Dubaish, 2012) or per volume (Carson *et al.*, 2013) all being provided.

3. *Microplastics in freshwater environments*

Thanks to the various studies conducted on microplastics, we have begun to generate a considerable body of knowledge on this pollutant in marine environments. Despite the widely reported fact that rivers and continental environments are a major source of marine microplastics, only limited knowledge is actually available on this contamination in lakes and rivers. The gap in knowledge is wide owing to the lack of: i) data related to the occurrence and associated effects of microplastic contamination in freshwater ecosystems; and ii) robust and accurate methodologies to assess microplastic concentrations in freshwater (environment and biota).

The remainder of this section will be based on a critical review published in *Environmental Chemistry* in 2015:

Dris, R., Imhof, H., Sanchez, W., Gasperi, J., Galgani, F., Tassin, B., and Laforsch, C. (2015). Beyond the ocean: Contamination of freshwater ecosystems with (micro-) plastic particles. Environ. Chem. 12, 539-550.

This review was intended to summarize available data on microplastics in freshwater ecosystems and proceeded to identify and discuss scientific challenges surrounding this issue. An update will be provided, complete with more recent published studies beyond our own. The corresponding results will be presented subsequently. The 2015 review examined first the sediments then the water column of rivers and lakes. The studies evaluated are listed below (Table 3). Although microplastic abundance in estuaries has not received much attention either (Browne *et al.*, 2010; Sadri and Thompson, 2014; Zhao *et al.*, 2014), only freshwater ecosystems will be considered herein since the strong influence of salinity gradients and tidal movements in these systems may have major consequences on microplastics dynamics.

Table 3: List of the studies reviewed relative to microplastic contamination in lakes and rivers, including the methods and units employed.

| | Year | Sites | Compartment(s) studied | Sampling methods | Identification-method | Units used | Reference |
|---------------|------|---|---|--|--|--|-----------------------------------|
| Lakes | 2011 | Lake Huron (Canada, USA) | Lakeshore sediments | Visual inspection and plastic particles | FT-IR | Particles.m ⁻² | (Zbyszewski and Corcoran, 2011) |
| | 2012 | Lake Geneva (Switzerland, France) | Lakeshore sediments Lake water | Manual collection of sediment samples Manta trawl | Visual inspection | Number of particles in 1-L samples Particles.km ⁻² | (Faure <i>et al.</i> , 2012) |
| | 2013 | Lake Garda (Italy) | Lakeshore sediments | Random grid sediment sampling | RM | Particles.m ⁻² | (Imhof <i>et al.</i> , 2013) |
| | 2013 | Lakes Superior, Huron and Erie (USA, Canada) | Lake water | Manta trawl | SEM/EDS | Particles.km ⁻² | (Eriksen <i>et al.</i> , 2013a) |
| | 2013 | Lake Geneva (Switzerland, France) | Lakeshore sediments Lake water | Manual collection of sediment samples Manta trawl | Visual inspection | Particles.m ⁻² Particles.km ⁻² and g.km ⁻² | (Faure <i>et al.</i> , 2013) |
| | 2014 | Lake Hovsgol (Mongolia) | Lake water | Manta trawl | Visual inspection | Particles.km ⁻² | (Free <i>et al.</i> , 2014) |
| | 2014 | Lake Erie and St. Clair (USA, Canada) | Shorelines | Manual collection of sediment samples | Randomly selected samples with FT-IR | Particles.m ⁻² | (Zbyszewski <i>et al.</i> , 2014) |
| | 2015 | Lakes Geneva, Constance, Neuchâtel, Maggiore, Zurich and Brienz (Switzerland) | Lake water Lakeshore sediments Biota (fish and birds) | Manta trawl (300 µm) Manual sediment samples - | FTIR-ATR - - | Particles.km ⁻² and m.km ⁻² Particles.m ⁻² and mg.m ⁻² - | (Faure <i>et al.</i> , 2015) |
| | 2015 | Lake Ontario (Canada) | Bottom sediments | Mini box corer | FTIR-ATR or RM | Number of items sampled | (Corcoran <i>et al.</i> , 2015) |
| Rivers | 2011 | Los Angeles and San Gabriel Rivers (USA) | River water | Manta net Streambed samples Hand net (0.8, 0.5 mm mesh size) | Visual inspection | Particles.L ⁻¹ | (Moore <i>et al.</i> , 2011) |
| | 2014 | Danube River (Germany, Austria, etc.) | River water | Stationary driftnets (0.5-mm mesh size) | Density separation & Visual inspection | Particles in 1,000 m ³ | (Lechner <i>et al.</i> , 2014) |
| | 2014 | St. Lawrence River (Canada) | Bank sediments | Grab samplers | Differential scanning calorimetry | Particles.m ⁻² | (Castañeda <i>et al.</i> , 2014) |
| | 2014 | Four Estuarine Rivers in the Chesapeake Bay (USA) | River water | Manta trawl | RM | g.km ⁻² | (Yonkos <i>et al.</i> , 2014) |
| | 2015 | Yangtze River and four tributaries (China) | River water | Nylon net (112 µm) | FTIR-ATR | Particles.km ⁻² | (Zhang <i>et al.</i> , 2015) |
| | 2015 | Rhine River (Germany) | River water | Manta trawl (300 µm) | FTIR-ATR | Particles.km ⁻² | (Mani <i>et al.</i> , 2015) |
| | 2015 | Rhône, Aubonne, Venoge and Vauchère Rivers (Switzerland) | River water | Manta trawl (300 µm) | FTIR-ATR | Particles.h ⁻¹ , mg.h ⁻¹ and particles.m ⁻³ | (Faure <i>et al.</i> , 2015) |
| | 2015 | Rhine and Main Rivers (Germany) | Bank sediments | Manual collection | FTIR-ATR | Particles.kg ⁻¹ of dry sediment and mg.kg ⁻¹ | (Klein <i>et al.</i> , 2015) |

3.1 Lake shore and riverbank sediment samples

a. Microplastic occurrence rates

Several studies have reported on the microplastic contamination of lakeshore, lake bottom and riverbank sediment samples from continental aquatic systems in Europe, North and South America, and Asia.

In the lakeshore sediments of Lake Garda (Italy), the authors reported that the north shore contained $1,108 \pm 983$ microplastic particles.m⁻², whereas only 108 ± 55 microplastic particles.m⁻² were observed on the south shore (Imhof *et al.*, 2013). The spatial distribution of microplastics suggests that wind, lake morphology and the strong currents are responsible for this observed pattern. The study found that the most abundant polymer (45.6%) was PS, while PE was highly abundant as well (43.1%). PA and PVC were also identified at sizes down to 9 µm. This study highlighted that the particles observed were fragments originating from the breakdown of larger particles (most likely post-consumer products), given that the scanning electron microscopy analysis revealed distinct signs of degradation.

Another study assessed microplastic contamination of lakeshore sediments along Lake Geneva (Switzerland) (Faure *et al.*, 2012). The results of this study were presented in terms of particles per liter of sediment; concentrations varied from 1 to 7 particles.L⁻¹, with the predominant polymer being PS. Microplastic concentrations during a second study of Lake Geneva lakeshore sediments (Faure *et al.*, 2013) ranged from 2,656.25 to 5,018.75 particles.m⁻², which was far greater than the highest concentration reported at Lake Garda. A predominance of textile fibers, representing more than 90% of identified microplastics, was observed in the latter study.

Microplastics were also detected in all samples from 19 different beaches on 6 Swiss lakes (Faure *et al.*, 2015). The mean concentration was $1,300 \pm 2,000$ particles.m⁻², or $920 \pm 1,500$ mg.m⁻²; the individual values ranged between 20 and 7,200 particles.m⁻², corresponding to 1-6,000 mg.m⁻². Foams (46%) and fragments (27%) were the most abundant shapes, followed by fibers (19%) and films (6%). Other shapes were counted in very small numbers. As for polymers, the proportions were given for surface waters and sediments together, resulting in 62% of PE, 15% of PP and 12% of PS.

In North America, the distribution of particles along the lakeshores of one of the Laurentian Great Lakes (Lake Huron, Canada/USA) has been studied (Zbyszewski and Corcoran, 2011). In

this work, particles were directly collected at the shoreline then separated into three groups: [< 5-mm plastic pellets], [> 5-mm broken plastic fragments], and [all sizes of PS particles]. The predominant form of microplastic on Lake Huron lakeshores was dependent upon sample location. At one sampled site, over 94% of observed plastic particles were industrial pellets, while at another site pellets made up only 15%, with the largest fraction consisting of PS foam. The majority of pellets, predominantly PE, were observed in the vicinity of an industrial zone.

In a second publication (Zbyszewski *et al.*, 2014), the abundance of plastics on the lakeshores of Lake Huron, Lake Erie and Lake St. Clair (Canada and USA) was assessed and compared with levels previously determined for Lake Huron. Like in the first study, a high number of pellets was reported in comparison to fragments and PS foam, especially at Lake Huron where 92% of the 3,209 particles were industrial pellets. The same was found for Lake Erie, with 39% of the 1,576 particles. Industrial pellets were more abundant adjacent to industrial areas and decreased along the shoreline. Along Lake Erie, PA was one of the main polymers observed, making up 33% of all plastic and arising mainly in pellet form (47% of all pellets). Compared to other studies, the observed abundance of plastic debris was rather low (Lake Huron: 4.75 ± 11.83 particles.m⁻², Lake Erie: 1.54 ± 1.01 particles.m⁻², Lake St. Clair: 1.72 ± 2.64 particles.m⁻²). This result might be due in particular to a restricted sampling of visible fragments and pellets, causing microplastics invisible to the naked eye to be overlooked. Nevertheless, the Great Lakes display a high degree of plastic debris contamination, most of which due to industrial pre-production pellets, i.e. accounting for 66% of the plastic load.

In general, the lakeshores of Lake Huron, Lake Geneva and Lake Garda contain lower concentrations than marine beaches known to be highly contaminated (Hidalgo-Ruz *et al.*, 2012). Lake Huron displays characteristics more similar to an ocean, hence with a plastic pellet concentration similar to that of marine systems (Derraik, 2002); this finding contrasts with Lake Garda or Lake Geneva, where only low pellet concentrations were reported. Local conditions and sources might explain some of these differences.

The bottom sediments of Lake Ontario were also considered (Corcoran *et al.*, 2015). In the samples analyzed, 35 microplastic particles were identified with none being found below a depth of 8 cm and with more particles being identified in the most recent sediments. Using the sedimentation rate, it was calculated that microplastics started to accumulate 38 years

ago. PE represented 74% of the number of particles, PP accounted for 17% and nitrocellulose (NC) 9%. Moreover, since these polymers are less dense than water, their sedimentation suggests that biofouling could be the cause of sinking particles.

The literature on microplastics in river sediments is quite sparse. A sediment study of the St. Lawrence River (Canada) revealed a relative abundance of microbeads, with sizes varying between 0.5 and 2 mm (Castañeda *et al.*, 2014). The targeted size range is rather large to produce an accurate view of microbeads. Even though the presence of microbeads was ubiquitous in all sediment samples (mean: 13.832 particles.m⁻²), some sites presented much higher concentrations (maximum: 105 particles.m⁻²). Such a spatial distribution is potentially explained by environmental factors affecting sedimentation.

Between 228 and 3,763 particles.kg⁻¹, corresponding to 21.8 and 932 mg.kg⁻¹ of dry sediment samples, were found on riverbank sediments of two rivers in Germany (Rhine and Main) (Klein *et al.*, 2015). The most widely represented size class was found to be the smallest, ranging from 63 to 200 µm, while the largest class was recorded in negligible concentration. Fibers, fragments, spheres and pellets were all encountered in the samples. The authors identified 74% of the particles as PS, 23% as PE and 15% as PP.

b. Sampling and separating microplastics from sediments

At Lake Garda, sediment sampling was performed using random grid samples (Imhof *et al.*, 2013). Microplastics were separated according to density using a zinc chloride (ZnCl₂) solution. To analyze the lakeshore sediment samples from Lake Geneva, two protocols were applied (Faure *et al.*, 2012, 2013). The first one consisted of a direct collection of coarse plastic fragments at the lakeshore, though the authors failed to specify the size of fragments collected. In the second protocol, sand samples were successively separated using 5 and 2-mm sieves, after which water was added to collect floating particles. In the 6 Swiss Lakes, sediments were collected on 0.3 x 0.3-m quadrats to a depth of 5 cm, resulting in 4.5 L of sample volume (Faure *et al.*, 2015).

At the sites on Lake Huron, Lake Erie and Lake St. Clair (Zbyszewski and Corcoran, 2011; Zbyszewski *et al.*, 2014), plastic fragments [< 10 cm] were sampled from sandy lakeshores with stainless steel trowels. Sampling at each location made use of 1-m wide stripes running from

the water to the vegetation line. These stripes were placed along a 60-m transect parallel to the shoreline spaced 10 m apart. Larger items were counted at each site but not collected. In order to sample bottom sediment cores in Lake Ontario, a mini box corer was deployed from a boat (Corcoran *et al.*, 2015).

A study of St. Lawrence River sediments relied on different types of grab samplers applied at depths varying from 10 to 15 cm (Castañeda *et al.*, 2014). A stainless steel spoon was used for Rhine and Maine riverbanks. The sampling area was 30 cm² wide and 2-3 cm deep (Klein *et al.*, 2015).

c. Identification

Sampled plastic particles from lakeshore and stream sediments have been identified as polymers by employing a variety of methods. In two studies, analysis was solely performed visually (Faure *et al.*, 2012, 2013). The nature of particles was most often determined by means of Fourier transform infrared (FT-IR) microspectroscopy (Faure *et al.*, 2015; Klein *et al.*, 2015; Zbyszewski and Corcoran, 2011; Zbyszewski *et al.*, 2014). The plastic particles observed in Lake Garda beach sediments have been analyzed using Raman microspectroscopy (Imhof *et al.*, 2013). One study actually introduced both Raman and FT-IR microspectroscopy, based on availability (Corcoran *et al.*, 2015).

An uncommon method for plastic particle identification was employed in a study assessing the abundance of microbeads in St. Lawrence River beach sediments, whereby the microbeads were analyzed using Differential Scanning Calorimetry (Castañeda *et al.*, 2014).

3.2 Water samples

a. Microplastic occurrence

Microplastic contamination of surface water has also been investigated, particularly in lakes. In Lake Geneva (Switzerland) (Faure *et al.*, 2012), the authors reported an extrapolated density of 48,146 particles.km⁻². Similarly, the surface water of the Laurentian Great Lakes (i.e. Lake Huron, Lake Superior, Lake Erie) has been sampled (Eriksen *et al.*, 2013b). Plastic particles have been categorized in three groups: [0.355 mm - 0.999 mm], [1.00 mm - 4.75 mm], and [> 4.75 mm]. Most particles have been observed in the smallest category, suggesting a similar risk for freshwater biota, as reported in marine environments (Cole *et al.*, 2011; Wright *et al.*, 2013). Several of the microplastic particles were green, blue and purple-colored spheres, likely stemming from facial cleaners and other personal care products; these were identified as PE and PP. The concentrations on the studied lakes averaged 43,157 particles.km⁻² and ranged from zero to 280,947 particles.km⁻². Lake Erie alone accounted for 90% of the total plastics reported in all three lakes and contained the two most contaminated zones. The authors suggest that this high abundance results from: converging currents, proximity to several coal-fired power plants, and their location downstream of cities such as Detroit and Cleveland.

In a remote mountain Lake (Lake Hovsgol, Mongolia), an average density of 20,264 particles.km⁻² (min-max values: 997 - 44,435 particles.km⁻²) was observed (Free *et al.*, 2014). The particles were grouped into the same three size classes as for the Laurentian Great Lakes. Though Lake Hovsgol is large with a surface area similar to that of Lake Erie, its catchment is less densely populated. Despite this difference, contamination by microplastic particles is still significant, a finding the authors attribute to aerial transfer from distant urban sources.

The concentrations of microplastics reported for rivers are highly variable, most likely due to the different methodologies applied. A study of the Danube River in Central Europe (Lechner *et al.*, 2014) revealed a mean (\pm standard deviation) plastic abundance of $316.8 \pm 4,664.6$ items.1,000 m⁻³ (0.00032 ± 0.00465 particles.L⁻¹) during a two-year survey (2010-2012) period. The corresponding plastic input via the Danube into the Black Sea was estimated at 4.2 t.day⁻¹. Industrial raw material (pellets, flakes and spherules) accounted for a substantial portion (79.4%) of the plastic debris.

A study conducted on Rhine River surface water (Mani *et al.*, 2015) showed an average of 892,777 particles.km⁻² with a peak at 3.9 million particles.km⁻² in the metropolitan area, which like for the study cited previously indicates a very high contamination level clearly explained by the high density of human population and activity. In this study, spheres were the most abundant shape (opaque: 45.2%, transparent: 13.2%), followed by fragments (37.5%) and just a few fibers (2.5%). PS was the most prevalent polymer (29.7%), with PP in second place (16.9%). PE was found in smaller proportions. Acrylate (9.3%), PES (5.1%) and PVC (1.7%) were also identified. The extrapolation step yielded a daily discharge of over 191.6 million microplastic particles into the North Sea. This estimation however is solely based on the first 0.18 m of depth. The data indicated no microplastics 5 m deep, thus confirming the relevance of focusing on surface water.

Another study investigated the surface water of both lakes and rivers. In all, 4 Swiss rivers and 6 Swiss lakes were considered (Faure *et al.*, 2015). All the rivers fed Lake Geneva, including the Rhone. This study also analyzed pollutants that were either adsorbed on or contained in microplastics. Results showed microplastic contents in all samples, with the number of small microplastics (< 1 mm) being 5.6 times greater than large particles. The mean density of microplastics in the lakes was 91,000 particles.km⁻², corresponding to 26,000 mg.km⁻². In the rivers, a rate of 790 particles.h⁻¹ was found, equivalent to 170 mg.h⁻¹ or 7 particles.m⁻³. Fragments (61%) and foams (14%) were the most commonly counted types in surface water. Films (13%) and fibers (10%) were also recorded in the counts. The characterization step revealed a prevalence of PE (62%), followed by PP (15%) and PS (12%).

Two California rivers (USA), i.e. the San Gabriel and the Los Angeles, were investigated (Moore *et al.*, 2011). Their plastic particle numbers ranged from 0.01 to 12.9 particles.L⁻¹. After a rain event, smaller microplastics (1 - 4.75 mm) were found to be 16 times more abundant in the Los Angeles River than larger particles (> 4.75 mm). Under the same conditions, smaller particles were only 3 times more abundant in the San Gabriel River. In both rivers, 71% of the plastic items recovered were foam-based. An extrapolation of these results estimated that 2.3 billion particles had been introduced into the marine environment over a 3-day period.

Concentrations of microplastics in the North Shore Channel in Chicago (USA) were measured both upstream and downstream of a waste water treatment plant (WWTP) outlet (i.e. the

Terrence J. O'Brien Water Reclamation Plant) (McCormick *et al.*, 2014). A mean concentration of 1.94 particles.m⁻³ (0.00194 particles.L⁻¹) was observed upstream of the WWTP, while 17.93 particles.m⁻³ (0.01793 particles.L⁻¹) were recorded downstream. These results suggest that WWTP discharges might represent a major primary source of microplastics in freshwater.

In the Chesapeake Bay (USA), concentrations reached a mean of 246 g.km⁻², corresponding to 260,000 particles.km⁻², in one of the four estuarine rivers examined (Yonkos *et al.*, 2014). These concentrations demonstrate statistically significant, positive correlations with population density and the proportion of urban/suburban development within watersheds. Let's note that the greatest microplastic concentrations also occurred shortly after major rain events at three of the four sites.

Another paper has focused on surface water contamination in the Three Gorges Reservoir in China (Zhang *et al.*, 2015). Five samples were gathered in the main stream of the Yangtze River, and 4 samples were extracted from the estuarine areas of four of its tributaries. Results reported a density ranging from 3,407.7 x 10³ to 13,617.5 x 10³ items.km⁻² in the Yangtze and from 192.5 x 10³ to 11,889.7 x 10³ items.km⁻² in its tributaries. This contamination level is extremely high and has been correlated with the high population density and extensive human activity on the catchment. The most abundant size class was between 500 µm and 1.6 mm (30% - 57%). The authors noted an increase in microplastic density towards the dam, where water flow is reduced and human activity more intense. After characterization, PP was found to be the most common polymer (36.79% - 57.12%), along with PE (42.14% - 63.21%). PS was found on occasion (0% - 12.7%). These microplastics were in the form of either sheets, lines, foam or fragments.

b. Surface water sampling

Like in marine environments, manta trawl sampling is the primary method employed for lake surface water or, more recently, for river water. In Lake Geneva, a 333-µm mesh manta trawl was utilized (Faure *et al.*, 2012, 2013). The samples were then passed through a 5-mm sieve in order to separate out the macro- and microplastics. Other studies focusing on lake water contamination by microplastics also introduced a 333-µm net to collect samples (Eriksen *et al.*, 2013a; Faure *et al.*, 2015; Free *et al.*, 2014).

Manta trawls (333 μm) have also been used (Mani *et al.*, 2015; McCormick *et al.*, 2014; Moore *et al.*, 2011; Yonkos *et al.*, 2014) to sample river surface water. Other types of nets/devices have also been adopted for rivers, namely: streambed samplers and hand nets (sampling surface water - < 1-mm mesh size) (Moore *et al.*, 2011), stationary driftnets (sampling the top 0.5 m of the water column - 500- μm mesh size) (Lechner *et al.*, 2014), and nets towed on the side of a boat (sampling surface water - 112- μm mesh size) (Zhang *et al.*, 2015).

c. Organic matter removal

Despite the fact that organic debris hampers the identification of plastic particles and especially microplastic particles, only three studies treated the samples prior to analysis. Two of them applied a wet oxidizing protocol with hydrogen peroxide in the presence of an iron(II) catalyst in order to remove organic material from the river or lake water samples (Free *et al.*, 2014; Yonkos *et al.*, 2014). Another study used an enzymatic treatment that called for putting different enzymes (including cellulase and chitinase) into river samples (Mani *et al.*, 2015).

d. Identification

Plastic particles observed in surface samples from lakes and streams have been identified as polymers in ways similar to particles detected in lakeshore sediments. Although the identification by visual means is less reliable, it has still been chosen in many studies (Faure *et al.*, 2012, 2013; Free *et al.*, 2014; Lechner *et al.*, 2014; Moore *et al.*, 2011). FT-IR microspectroscopy has been used on three occasions (Faure *et al.*, 2015; Mani *et al.*, 2015; Zhang *et al.*, 2015). Raman spectroscopy was preferred in another study (Yonkos *et al.*, 2014).

3.3 Biota samples

While microplastics in freshwater have admittedly received less attention, even fewer studies have assessed the freshwater biota ingestion of microplastic particles. The first was performed in Lake Geneva (Switzerland): the gut contents of 21 adult northern pikes (*Esox lucius*), 18 common roaches (*Rutilus rutilus*) and 2 common breams (*Abramis brama*) were analyzed, yet without finding any plastic fragments (Faure *et al.*, 2012). The second study assessed microplastics in the gut of wild gudgeons (*Gobio gobio*) sampled in 11 French rivers (Sanchez *et al.*, 2014). For this purpose, fish guts were dissected and subjected to direct visual inspection under a dissecting microscope. Microplastics, defined as hard and colored fibers, were observed in fish from 8 rivers, at an occurrence rate of between 11% and 26%. The

authors demonstrated that fish from urban rivers were more highly contaminated with microplastics than those collected in rivers with low anthropogenic impact. This study confirms that freshwater fish do ingest microplastics and moreover supports the need for further studies to characterize microplastic contamination of river and lake biota. Both studies used visual inspection methods to identify the plastic particles and fibers.

Microplastics were also discovered in the digestive tracts of terrestrial birds in Shanghai (China). Fibers were predominant in comparison with fragments (Zhao *et al.*, 2016). This study identified 136 natural fibers, 200 synthetic fibers and 28 fragments in 16 organisms. The decline in the proportion of natural fibers from esophagus to stomach to intestine suggests that these particles could be digestible. For purposes of this study, a natural fiber is assumed to include both natural and man-made fibers. The authors call for further research on the effects of natural fibers given their potential to be associated, as is the case for synthetic fibers, with a 'cocktail of chemicals'. Such chemicals include dyes, additives and pollutants adsorbed from the environment. One of the dyes often used in association with cellulose (i.e. Direct Red 28) was, for instance, proven to be a carcinogen for vertebrates (Remy *et al.*, 2015).

3.4 Challenges and recommendations

One of the major challenges inherent in microplastic research is the need for general definitions and methodological standardization. Such improvements will enable drawing comparisons of results across studies and sites and moreover should encompass every step involved in the microplastic investigation, i.e. sampling, sample processing, identification, and final statistics.

a. Definition of microplastics and units used

Microplastics comprise a heterogeneous assembly of pieces varying in size, shape, color, specific density and chemical composition. The microplastic size definition has varied in previous marine studies. This heterogeneity is also found in studies on the continental environment. To avoid this inconsistency, it is important to provide a common definition of microplastics that would support establishing a standardized sampling method and enhancing compatibility between future studies. In the marine context, studies consider microplastics as particles smaller than 5 mm (Arthur *et al.*, 2008; Hidalgo-Ruz *et al.*, 2012). However, given the

possible uptake by different aquatic organisms as well as the handling step during extraction and identification, it has been suggested to narrow the term microplastic to particles that can be optically identified with the naked eye and handled with tweezers, yet which remain impossible to handle individually or distinguish without optical tools (e.g. microscope, stereo microscope). This distinction has been made by several authors of both marine studies (Eriksen *et al.*, 2013b; Hidalgo-Ruz *et al.*, 2012) and limnetic studies (Eriksen *et al.*, 2013a; Free *et al.*, 2014; Imhof *et al.*, 2013). Similarly, the Technical Working Group tasked with developing suggestions for implementation of the Monitoring of Marine Litter for the Marine Strategy Framework Directive proposed a separation between microplastic > 1 mm and microplastic < 1 mm, based on the aforementioned reasons (Galgani *et al.*, 2010).

In addition to offering a different microplastic definition, studies often list their results in different units, thus rendering any comparability practically infeasible. This inconsistency mainly stems from the differing sampling, extraction and identification methods.

Studies assessing lakeshore sediments use particles per volume (Faure *et al.*, 2012) or per sampled surface area (Imhof *et al.*, 2013; Zbyszewski and Corcoran, 2011). Such units are comparable with marine studies, although the latter also provide measurements of particles per sediment weight (Hidalgo-Ruz *et al.*, 2012).

For lake samples, concentrations are indicated in particles per surface area (Eriksen *et al.*, 2013a), which once again is comparable to marine surface water sampling (Hidalgo-Ruz *et al.*, 2012). For river data, particle abundance is typically reported as particles per water volume (Lechner *et al.*, 2014; McCormick *et al.*, 2014; Moore *et al.*, 2011). It is possible at times however to calculate from one unit to the other, but the information required must be provided as well. We are also suggesting that the velocity of water entering the net should be systematically measured and given.

To properly identify plastic sources and characteristics, studies should categorize plastics into different shape/size classes. Separating fibers (1 dimension larger than the other two), fragments (2 dimensions large relative to a third smaller one) and spherules (similar order of magnitude for all 3 dimensions) would enhance comparability among the various sites.

b. Sampling methods

Sediment sampling

Accurate and representative sampling of an adequate matrix constitutes the first step to assessing environmental contamination. Unfortunately, the same methodological divergence observed in marine systems (for a review, see Hidalgo-Ruz *et al.* (2012) occurs in sampling methods used for lakeshore sediments. Sampling differs not only in the methodologies employed and volumes sampled, but also in the locations sampled. To avoid local heterogeneities, we are proposing a sampling approach that relies on sediment core samples (diameter: 10 cm, depth: 5 cm) extracted along a 20-m transect (e.g. along the drift line of a lake system) spaced 2.5 m from one another, which would result in a sample volume of 4 - 6 liters. For rivers, a different methodology should be applied: instead of running parallel to the waterline, the riverbank could be divided into three short 5-m transects extending over the accumulation zone perpendicular to the waterline.

Water sampling

To date, any comparison between results from different studies proves to be nearly impossible due to the use of nets with differently-sized meshes. Moreover, river water has been sampled from varying positions, in terms of both sampling depth and distance from the riverbank. The main challenges facing method standardization are: i) the spatiotemporal frame; and ii) the implemented mesh size, which controls the smallest particle size capable of being sampled. A 300 - 333 μm mesh size is common in marine plastic and plankton research, by virtue of offering a tradeoff between good handling and larger fragment accumulation (which winds up clogging the net). Using a 300-333- μm mesh in the freshwater environment would enable comparing data gathered from both marine and continental environments. The use of a manta trawl however may lead to underestimating microplastics within a size range smaller than the mesh size (Norén, 2007). To broaden the view of plastic contamination, we suggest using nets with a smaller mesh size or, whenever necessary, even resorting to bulk water sampling. This consideration should be taken seriously, especially given that the smallest particles present the greatest risk of being ingested.

Sampling microplastics on the surface of inshore waters may entail certain technical difficulties relative to marine ecosystems. In contrast with more nutrient-poor marine

ecosystems, inshore waters display an amount of organic matter that tends to be much higher, especially during periods of algal bloom or leaf fall in autumn. In addition, during high water periods, suspended matter, clay minerals and allochthonous inputs of organic material increase the risk of clogged nets, which might limit sampling duration and thus considerably reduce both sampled volumes and sample representativeness. Consequently, while towing a manta trawl seems optimal for marine water sampling, the net configuration might have to be modified in order to sample lakes and streams.

As opposed to lakes, rivers present a permanent water flow, and the current velocity must be taken into consideration to facilitate surface sampling. The current velocity can be either too slow (< 0.1 m/s) or far too fast, with the latter condition resulting in a high ram pressure that hampers net inflow. River water sampling may be performed from a fixed position. A second problem arises from the need for a reference parameter yielding either the number of particles per surface or per volume. When in standing water, the length of the manta tow carried out can be used to calculate either the sampled volume or surface area, whereas in running water, a current velocity estimate must be determined using a flowmeter.

Furthermore, to determine a microplastic flux in running water, it is important to identify both the spatial and temporal variabilities of plastic particles, along with their dynamics in the river (i.e. distribution along the water column, sedimentation).

c. Sample processing

Separation of plastic polymers from inorganic/mineral materials

Should plastic particles be directly collected at the lakeshore or riverbank, it is very likely that microparticles will be overlooked. A crucial step to ensuring all plastic particles have been taken into account therefore consists of extracting microplastics from bulk environmental samples. Various density separation methods can be used to separate microplastics from sediments. The methodology selected can account for a large share of uncertainty in the success of recovery. Due to their surface properties, microplastics can attach to any contact surface. The number of working steps should thus be reduced for the density separation process applied to microplastics. Since sample preparation and particle identification are both time-consuming, this procedure must be optimized as regards the extraction method.

Several methods have been developed for this purpose. With the Munich Plastic Sediment Separator, a sample volume of up to 6 L can be analyzed in a single run (Imhof *et al.*, 2012); it offers a high microplastic recovery rate, especially for small particle sizes (under 1 mm). Other methods involving elutriation, followed by density separation and fluidization, also proved to be efficient (Claessens *et al.*, 2013; Nuelle *et al.*, 2014). Protocols can be adapted to optimize microplastic recovery rates in different types of sediments (sandy or clayey soils, biota-rich sediments, etc.).

Depending on the density of the solution chosen for the separation step, the range of recovered polymers differs by a wide margin. Previous studies on marine or estuarine environments have mainly used a sodium chloride solution (NaCl - 1.2 kg.L^{-1}) (Hidalgo-Ruz *et al.*, 2012). If all commercially produced polymers were recovered, the solutions introduced for future separations must have a density at least equal to 1.5 kg.L^{-1} (Imhof *et al.*, 2012). Use of a higher-density solution takes into account both the potential additives capable of increasing particle density and the attached biota or organic particles. Some recently suggested separation fluids are zinc chloride (ZnCl_2 - 1.6 to 1.7 kg.L^{-1}) (Imhof *et al.*, 2012) and sodium iodide (NaI - 1.6 kg.L^{-1}) (Claessens *et al.*, 2013; Nuelle *et al.*, 2014), both of which are relatively inexpensive yet have the drawback of being moderately toxic for the biota. The separation fluid may be used more than once, by virtue of being easily recovered with, for example, candle filters. A more expensive method calls for using a non-toxic polytungstate solution of a density reaching 2.0 kg.L^{-1} (Zbyszewski and Corcoran, 2011).

Removal of organic matter

The separation of plastic particles from other organic materials (such as shell fragments, small organisms, algae or sea grasses, and tar) has been shown to be necessary for marine matrices and, to a greater extent, for continental environment matrices. These latter matrices contain more organic material, especially in the case of eutrophic lake and streams. Performing a density separation alone to isolate plastic particles from sediment samples proves to be inefficient in reducing natural organic debris, hence treatment methods must be applied to facilitate plastic particle identification. Several oxidation agents such as hydrogen peroxide (H_2O_2) (Mathalon and Hill, 2014), strong acids such as nitric acid (HNO_3) (Van Cauwenberghe and Janssen, 2014), hydrochloric acid (HCl) and mixtures of sulfuric acid (H_2SO_4) with H_2O_2

(Imhof *et al.*, 2013) were applied to remove organic material for limnetic, but also marine, samples. Methods utilizing strong acids must be avoided however since they affect and degrade plastic polymers (Claessens *et al.*, 2013). Alternative, anti-organic treatments therefore need to be developed. A wet oxidizing protocol was recently applied in a variety of studies, but the extent of degradation induced by such a protocol has yet to be analyzed.

Enzymatic digestion methods may prove to be more useful in removing organic matter without affecting plastic polymers. In 2014, an enzymatic protocol for marine water samples was published, revealing that 97% of organic material can be digested without damaging microplastic particles (Cole *et al.*, 2014). This digestion step can be conducted on bulk samples or after density separation of the sediment samples.

Quality assessment/Quality control

To develop a common protocol for sampling, extracting and identifying microplastics in freshwater ecosystems, QA/QC (Quality assessment/Quality control) approaches are very useful to: ensuring the quality of results, evaluating sources of variability and error, and increasing the level of confidence in the data collected. During sample processing, sampling and laboratory blanks that undergo the same analytical protocols should be introduced. Caution must be exercised when wearing synthetic fiber clothing, which should be avoided during sampling, extraction and further processing through to identification. Samples must be covered in order to prevent airborne contamination. Plastic extraction recovery techniques also need to be validated using, for example, sediments spiked with artificially placed plastic fragments. The impact of all organic matter removal methods on artificial polymers must be further examined. Moreover, the identification methods used should correspond to the size of the particles being analyzed.

Identification of polymers

Counting and identification are critical steps to addressing microplastic contamination. Visual observation has frequently been applied to assessing microplastic size and quantity. However, a pure visual examination using light or electron microscopy cannot reliably distinguish between polymers and other particles or determine the actual polymer type. This method may lead to overestimating plastic polymer contamination. In one study, nearly 20% of particles less than 1 mm that had initially been identified as microplastic by visual observation

were later found to be aluminum silicate from coal ash (Eriksen *et al.*, 2013a). Visual characterization and identification should thus be systematically coupled with a characterization technique. Reliable identification results are achieved with spectrometric methods such as FT-IR microspectroscopy and Raman microspectroscopy, or for some polymers with SEM/EDS (scanning electron microscopy / Energy Dispersive X-Ray Spectrometer) (Rocha-Santos and Duarte, 2015). Pyrolysis followed by GC-MS can also be applied (Fries *et al.*, 2013; Nuelle *et al.*, 2014), though all information on particle shape/size is lost.

Large microplastics can be handled with tweezers and therefore easily placed under the ATR crystal of a FT-IR, under a Raman or electron microscope, be inserted in Pyrolysis GC/MS, or prepared for Differential Scanning Calorimetry. Small microplastics need to be captured on matrices (e.g. filters) and subsequently undergo either manual or automated identification protocols using FT-IR or RM. Manual identification methods are highly time-consuming.

4. Urban inputs of microplastics

Plastic sources are often discussed in the literature with respect to marine plastic pollution. Direct sources, such as coastal tourism, recreational and commercial fishing, marine vessels and marine industries (aquaculture, oil rigs), are typically cited (Cole *et al.*, 2011) as major inputs.

In an urban context, various microplastic inputs into freshwater can be noted. The atmosphere, runoff and disposal of water treated by WWTPs are the most likely sources of microplastics. Our current knowledge of these sources remains quite limited.

As regards atmospheric inputs, no clear data exist. The role of the atmosphere was suspected when microplastics were observed in remote areas like Lake Hovsgol in Mongolia (Free *et al.*, 2014). Similarly, to the best of our knowledge, no study has focused on the microplastics in runoff, and the contribution of this source has not been estimated. In addition to the atmospheric microplastics washed away by rain and the dry accumulation on surfaces, a study has suggested the presence of microplastics in runoff stemming from automobile tires, building materials and road paints (Norwegian Environmental Agency, 2014). This study's findings remain conjecture, and such particles have yet to be observed in urban runoff.

On the other hand, several studies have considered WWTP disposal as a source of microplastics in rivers. It has been shown that laundry washing machines discharge a large amount of plastic fibers into wastewater, with one study estimating that a single garment releases in a single wash up to 1,900 fibers (Browne *et al.*, 2011). These fibers will most likely be subsequently found in wastewater. The same study indicated an average of 1 fiber.L⁻¹ in effluent discharged from a tertiary-level WWTP.

A mere three years later, the first studies assessing microplastics in wastewater and through WWTPs were published. One study investigated the removal efficiency within a WWTP located in the Helsinki Metropolitan Area (Talvitie *et al.*, 2015). The influent contained 180 textile fibers and 430 fragments per liter. After treatment, only 5 fibers and 9 fragments per liter remained in the effluent. This study raised a major issue regarding microplastic analyses in wastewater. The study samples were filtered through three filters, with respectively 200 µm, 100 µm and 20 µm mesh sizes. Despite this step, it was impossible to efficiently analyze more

than 300 ml per sample. Even if the clogging problem had been mitigated by using a series of filters, making it possible to filter up to 1 L, the final samples were full of organic material, thus preventing the observations and visual identifications performed during this work.

A secondary WWTP (serving 650,000 population equivalent) was sampled at various stages in a study in order to characterize the microplastic removal capacity (Murphy *et al.*, 2016). With the effluent containing an average of 15.70 particles.L⁻¹, it was reduced to 0.25 particles.L⁻¹ in the outlet, for a decrease of 98.41%. A significant proportion of the microplastics were eliminated during the grease removal step. Flakes (68%) and fibers (19%) were the predominant type found. While this study was able to treat greater volumes than the previous one, an underestimation of fibers could be attributed to the fact that prior to treatment the samples were passed through a 65- μ m sieve. This study has also highlighted the fact that microbeads were only found in grease samples; these microplastics could be totally retained during the grease removal step.

Until now, the most significant study dealing with microplastics through WWTP seems to be the one published by Carr *et al.* in 2016: it sampled effluents at 8 different facilities, with removal efficiencies between 95% and 99%. In agreement with the study by Murphy *et al.*, this recent work shows that microplastics are efficiently removed during skimming (grease removal) and settling treatment processes (Carr *et al.*, 2016). The microplastics identified in this study had similar profiles to the blue PE particles used in toothpaste formulations. The interest of this study lies in the sampling of over 0.18 million liters for each effluent, which constitutes a very large and representative volume. Its drawback pertains to use of an assembled stack of sieves with mesh sizes down to 45 μ m. Knowing that fibers typically possess a smaller diameter, it can be assumed that fibers have been underestimated, especially the smallest specimens, which could easily pass through the WWTP facilities.

In comparing the three studies, it appears that the main challenge consists of being able to filter large volumes of WWTP influent and effluent. The studies used sieves or filters with different mesh sizes, thus rendering any comparison infeasible. Surprisingly, none of these works applied treatments to remove organic matter, as was observed in the studies dealing with sediments, freshwater or biota. Such a solution should have been investigated in order to facilitate filtration and identification without having to use very large meshes.

Although the extent of removal varies from one study to the next, they all agree on the fact that WWTPs effectively reduce microplastic contamination. All authors indicate however that final contamination levels in the effluent are high enough to potentially affect receiving environments. This was demonstrated by a study sampling upstream and downstream of a treatment plant (McCormick *et al.*, 2014) (see Chapter 1, Section 3.2). Further work is needed to better determine the importance of this contribution compared to other sources.

WWTP removal raises questions over the fate of these microplastics. Before the studies cited herein, synthetic fibers were known to contaminate sewage sludge, even if data on precise contamination levels were lacking (Habib *et al.*, 1998; Zubris and Richards, 2005). This observation suggests that the use of sewage sludge for agricultural fertilization might significantly contribute fibrous microplastics into agrosystems. Moreover, plastic mulching could be another terrestrial source of microplastics, but to the best of our knowledge, these pathways have not yet been sufficiently documented (Rillig, 2012).

III. Conclusions

The exponential increase of plastics production during the last century, along with society's growing tendency to simply throw waste away, has led to an issue of worldwide importance. Plastic debris is ubiquitous and its presence has been demonstrated across the globe. Massive debris piles have raised aesthetic concerns and caused severe impacts on fauna. A very serious issue came to the fore with the breakdown of this debris into considerably smaller particles, so-called microplastics. These pollutants, which can also be manufactured at the microscopic scale, represent a far greater threat to biota since they can be ingested by a wide variety of species. For ecotoxicological purposes, they have been defined as plastic particles smaller than 5 mm.

In this chapter, the sudden gain of knowledge on plastic pollution over the past decade has been highlighted (Figure 10). These advances do not necessarily mean that the issue has been totally understood, as further work is still necessary. Many gaps in knowledge and key challenges have appeared and should be urgently addressed (Figure 11).

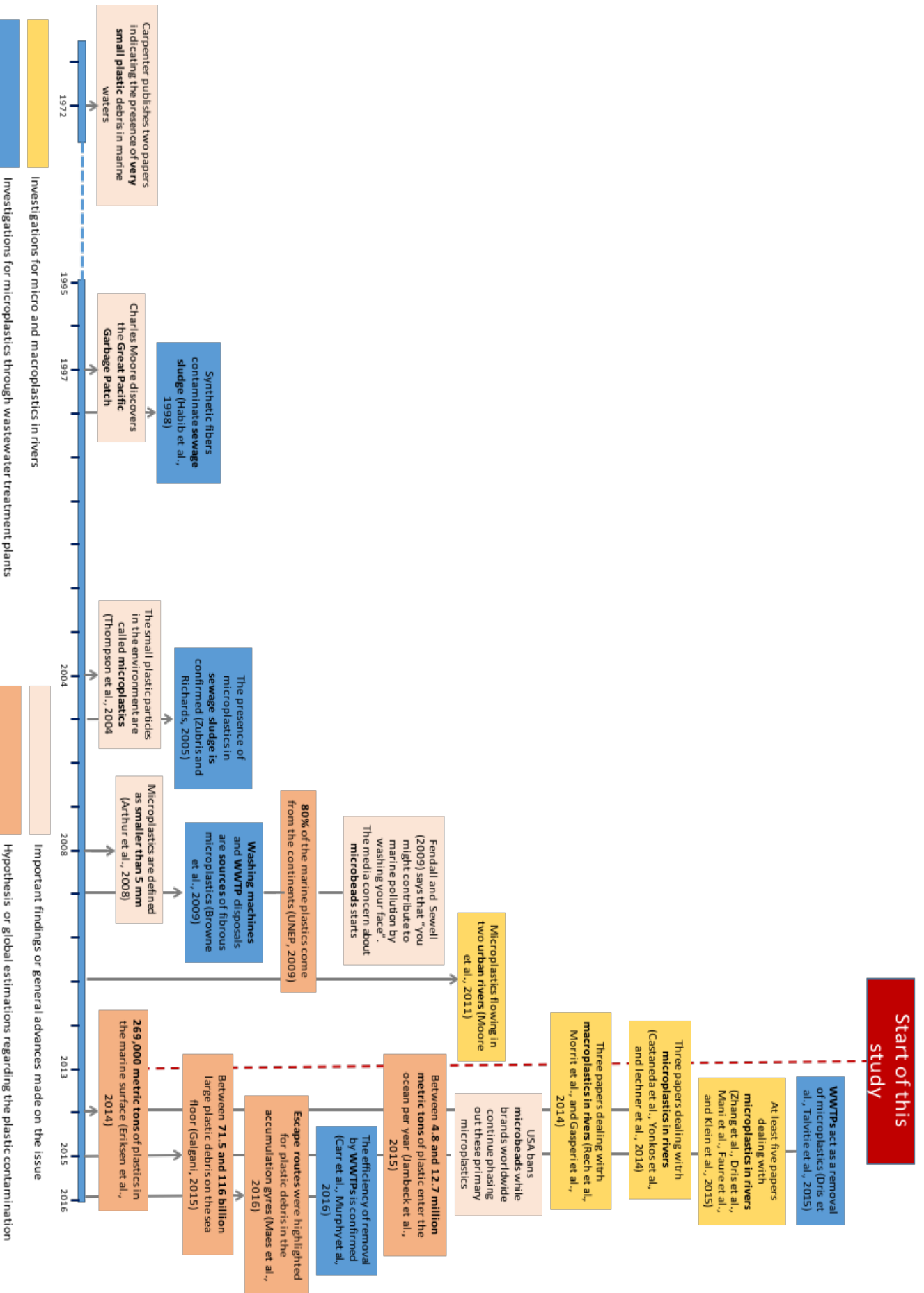


Figure 10: Key advances and dates relative to the issue of plastic pollution (to avoid overloading the timeline)

As has been summarized in this chapter, recent studies demonstrate a level of freshwater contamination nearly equal to that reported in the oceans. It is of utmost importance therefore to elucidate the sources, fate, fluxes and impact of microplastics and associated chemicals in freshwater ecosystems.

Sampling, separation and identification methods are key steps for an accurate characterization of microplastic contamination. The methods described in the existing literature however are very diverse, and no common methodology has emerged; this trend is most likely due to the novelty of the topic and it is not astonishing given that many of the studies were pilot projects. The constraint imposed is the limited comparability among studies using different methods. This methodological heterogeneity might be intrinsically more pronounced for freshwater (especially in rivers) due to the myriad of parameters related to freshwater sampling (river flow, season, type of net, position of the net or manta trawl, water column height, dynamic vs. static sampling, time of exposure, presence of suspended matter, plant debris, etc.). This situation could introduce various constraints leading to the use of alternative methods. The development of an improved, automated and standardized methodology to detect and identify microplastics appears to be a real challenge but must nonetheless be considered a priority in order to improve comparability between future studies (in both continental and marine environments). Comparable data on the contamination of various habitats are key to a reliable risk assessment, which will be needed for adequate mitigation and prevention measures in the future. Gaps however must be identified and challenges overcome as preliminary steps (Figure 11).

| Gaps | Main challenges |
|--|---|
| Definitions | |
| <p>There is no bottom limit to the definition of the microplastics</p> <p>The nanoplastics concept is unclear</p> | <p>It is crucial to make the results more comparable by fixing the bottom limit definition and making it less method dependent (cut off of the nets, sieves and filters used).</p> <p>All works should always use the definition of microplastics being smaller than 5 mm.</p> |
| Macro and microplastics in the oceans | |
| <p>How much (in mass and number) plastics come from the continents?</p> <p>How much float in the oceans?</p> <p>How much sink and accumulate on the sea floor?</p> | <p>The spatio-temporal heterogeneity at both large and regional scales should be refined</p> <p>Now that we start having many data on local contaminations, modals and global estimations should be made.</p> <p>The amount of mismanaged plastics should be more accurately estimated.</p> <p>The fragmentation, degradation and transport mechanisms and dynamics as well as the sinking rates and processes need more investigations. This works need to take into account the complete spectrum of sizes, shapes and polymers.</p> |
| Impact of microplastics | |
| <p>Some works indicated the translocation of the microplastics but this is highly questioned and need to be clarified.</p> <p>Potential effects and mortality rates are still very poorly documented.</p> <p>The role of the additives and the adsorbed chemicals are not yet understood and plainly evaluated.</p> | <p>Studies should be carried out with more environmentally realistic concentrations, oppositely to the very high exposure levels used to date.</p> <p>As for the mechanisms, the exposure experiments should include all microplastic categories, and not only the widely tested virgin PS, PE or PVC very small microbeads.</p> <p>The impact of the adsorbed chemicals should be evaluated in a more realistic context, which is with the presence of contaminated natural suspended matter. It would provide a more correct vision on the contribution of the microplastics as a pathway of pollutants into the organisms.</p> |
| Microplastics in freshwater | |
| <p>There is no homogenized methods to estimate accurately freshwater contamination.</p> <p>Aside from preliminary works on WWTPs, almost nothing is known on the sources and inputs of these plastics.</p> <p>Pathways, mechanisms and dynamics that affect the occurrences of microplastics in freshwater are unknown</p> | <p>Long term monitoring studies are needed in rivers. Similarly, small scale spatio-temporal variabilities would help understand the dynamics.</p> <p>Understanding the behavior and sinks of plastics (both micro and macro) in rivers would help quantifying the loads.</p> <p>Studies with homogenized methods are needed worldwide on rivers with different contexts (urban vs non urban, low vs high water flow etc.) to a better understanding and global estimation.</p> |

Figure 11: Major gaps in knowledge that were identified through the review presented in this chapter and some primary challenges with eventual recommendations for future work.

Chapter 2: Description of the study sites and methods used to quantify and characterize plastics



View of Paris from the Saint-Jacques Tower by Yann Caradec

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I. Description of the study sites

The study sites are located in the Seine River Basin. The Seine River is 777 km long from its source in the Côte d'Or department to its estuary at the city of Le Havre. The basin surface area equals 78,910 km². The Seine River is characterized by a relatively low water flow, making it easily altered by catchment activities, especially urban activities. The river crosses the Paris agglomeration, where it receives two incoming tributaries (Marne and Oise Rivers), the effluent from several wastewater treatment plants (WWTP) (20-22 m³.s⁻¹) as well as discharges during wet weather periods (runoff, combined sewer overflows, etc.).

The mean daily water flows of the Seine River through Paris, as recorded during 2014 and 2015, are plotted in the figure below (Figure 12). This flow varied from 86 m³.s⁻¹ to 1,050 m³.s⁻¹, with an average mean of 310 m³.s⁻¹.

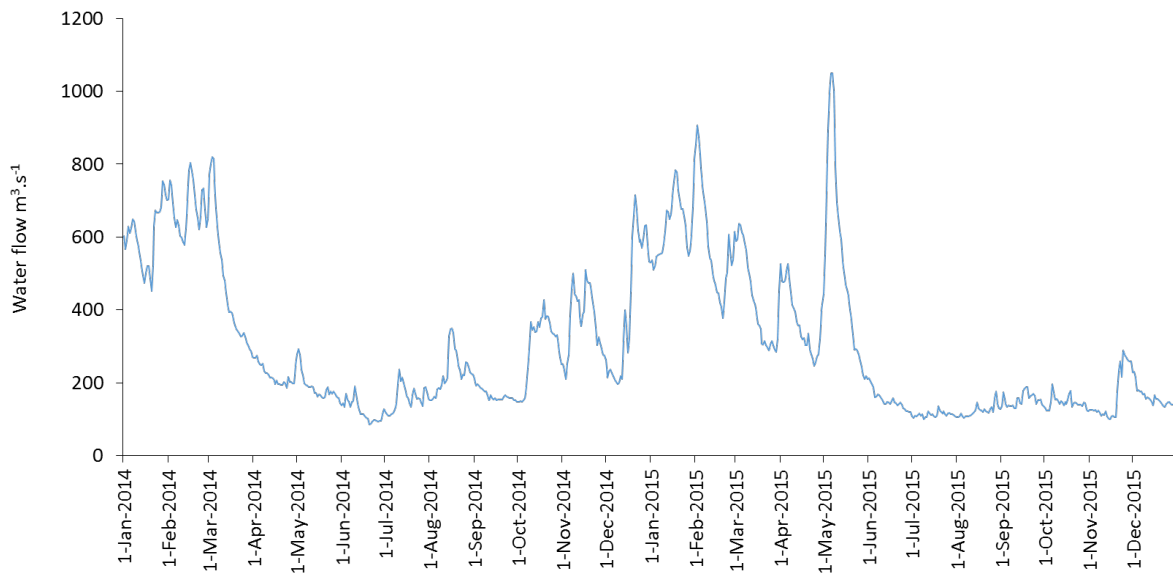


Figure 12: Seine River water flow in the city of Paris recorded at the Pont d'Austerlitz
(extracted from hydro.eaufrance.fr/selection.php).

The Paris agglomeration is located in the "Ile-de-France" Region administrative jurisdiction and provides the country's main economic center. According to the INSEE Statistical Office, this region's GDP (gross domestic product) ranks tops in France, accounting for 30% of the national GDP. Urbanized zones cover 24% of the region's total land area. The remaining areas are designated for agricultural activity (54%) and natural reserves (forestland and freshwater

- 22%). Even though agricultural uses occupy a large surface area, the urban activities (industrial and commercial) are the main contributors to GDP.

This study has focused more specifically on the Paris agglomeration (Figure 13). The Paris Metropolitan Area comprises a land area of 17,174 km² and a population of roughly 12.5 million (2013 statistics, INSEE - National Institute for Statistical and Economic Studies). The Paris agglomeration (i.e. conurbation) however is defined more restrictively. In just 2,845 km², it concentrates a large proportion of the population, with 10.5 million inhabitants, and therefore is a relevant site for observing the impact of intense human activity and strong anthropogenic pressures on freshwater sources.

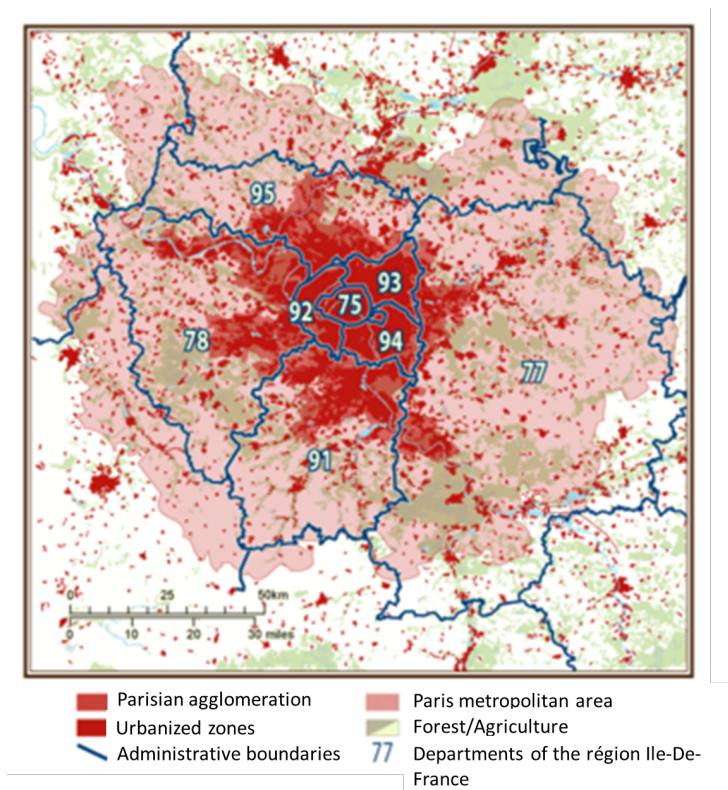


Figure 13: Delimitations of the Paris agglomeration, the Paris metropolitan area and the Ile-de-France Region.

While Paris constitutes this study's reference site, the decision was made to provide a comparison with the case of Ho Chi Minh City, as representative of the urban impact in a developing country. This comparison was performed in collaboration with the Asian Center for Water Research (CARE). Ho Chi Minh City is the economic capital of Vietnam and one of the most rapidly developing megacities in Southeast Asia with an official population of over 8

million. The increased economic, industrial and residential development in the city has tremendous consequences on the quality of the aquatic environment. Only 10% of the total municipal wastewater produced is treated with activated sludge (FAO, Food and Agricultural Organisation, 2014), the remainder being directly discharged into rivers and canals. Moreover, Ho Chi Minh City is located at the estuary of the Saigon River, giving rise to complex water dynamics due to tidal effects. In this context and considering the differences in waste management practices between industrialized and developing countries, a comparison between both sites has been carried out in this work.

II. Methods for qualifying and quantifying fiber and plastic contamination

As mentioned in the Introduction, the results of this research will be presented in three distinct chapters: Chapter 3 will focus on the case of macroplastics, Chapter 4 on microplastics in urban compartments, and Chapter 5 on microplastics in freshwater. This section will briefly discuss the methods employed in order to quantify and characterize plastic contamination. Due to inherent differences between compartments, the sampling protocol is matrix/compartment-correlated and had to be adapted for each compartment. To facilitate reading therefore, the description of sampling campaign protocols will not be provided herein but instead can be found in the corresponding sections. Moreover, the methods will only be described in this manuscript as they were actually carried out. A discussion of methodological pertinence and comparison with findings from the literature is available in Chapter 6.

Two distinct methods were developed for the macro- and microplastic analyses. Macroplastics are materials that can be handled and therefore visually and manually selected before being counted and weighed. They are chemically characterized at a later point. Microplastics underwent three steps after sample collection, namely: purification, observation (along with size and shape characterization), and chemical characterization (Figure 14).

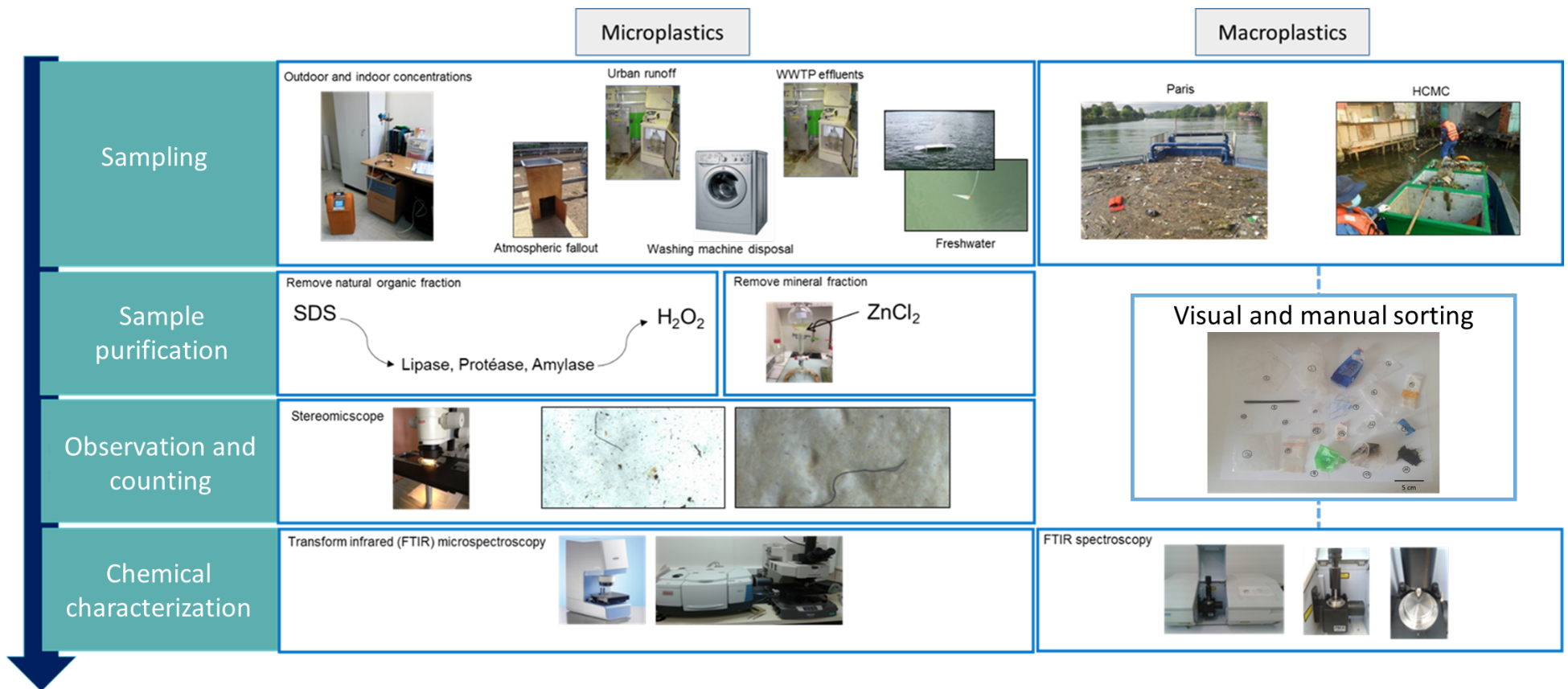


Figure 14: Schematic overview of the range of steps involved in qualifying and quantifying plastics in the various compartments.

1. Sample purification

1.1 Removal of natural organic matter

Samples are quite often biota-rich or highly concentrated in natural organic debris as well as mineral debris. These two fractions, given that they would hinder the following steps (filtration, observation and characterization), need to be removed.

Two protocols were tested in Seine River samples in order to select the one to be used for organic removal. Strong acids and bases, which were shown to alter microplastics, have therefore been excluded and not tested (Cole et al., 2014). The first protocol tested (i.e. Protocol A) was adapted from a method previously developed by a German team (Mintenig *et al.*, 2014); it consists of placing the samples consecutively in contact with various reactants so as to reduce the amount of natural organic debris. The first step calls for placing 1 gram of SDS (Sodium dodecyl sulfate), which is an anionic surfactant, in contact with the samples. After 24 hours in 70°C, 1 ml of biozyme F (containing lipase) and biozyme SE (containing protease and amylase) were added to the samples, which were subsequently incubated at 40°C for over 48 hours. Any material of a biological origin was then further reduced with 15 ml of hydrogen peroxide (30% H₂O₂) at 40°C for 48 hours. The samples had to be homogenized from one step to the next.

The second protocol (B) was first developed for marine environment samples and biota sample digestion (Cole et al., 2014). Since the organic materials encountered in continental environments are different, the validity of this protocol had to be tested, beginning by completely drying the samples in an oven at 70°C. A homogenous 15-ml solution was then added to the samples along with 6 ml of Tris-HCl (400 mM), 1.8 ml of EDTA (60 mM), 7.2 ml of NaCl (105 mM) and 150 mg of SDS (1%). The samples were heated at 50°C for 15 minutes before adding proteinase K (500 µg.ml⁻¹); next, they were incubated with the proteinase for 2 hours at 50°C. As a final step, sodium perchlorate (NaClO) was introduced and the samples were left at room temperature for over 20 minutes and then at 60°C for another 20 minutes.

For both protocols, filters were observed at each step. Seven samples were extracted from the same site and the same time in the Seine River on 16th June 2014. One sample was filtered without removing any natural organic matter. Three samples were tested according to

Protocol A, with each one being stopped at a different step of the protocol. The other three samples were similarly tested according to Protocol B (Figure 15).

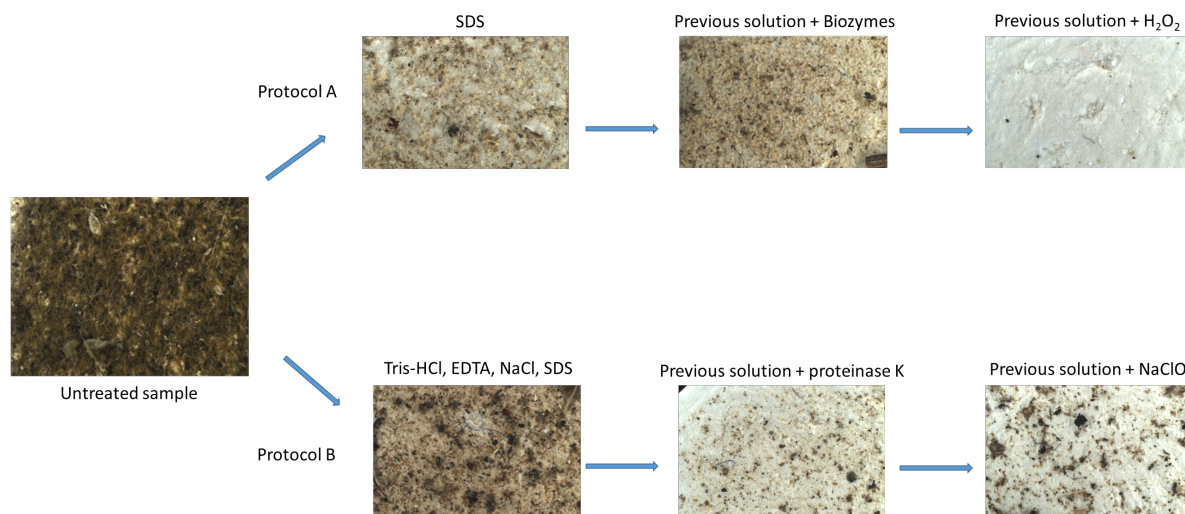


Figure 15: View of the filter surface with a stereomicroscope, showing the effect of various organic matter removal methods.

Removing natural organic matter is critical for freshwater samples, as demonstrated by the observation of non-purified samples. The use of SDS and biozymes exhibits a reduced amount of debris on the filter. H_2O_2 proved to be the most efficient for obtaining very clean filters with a considerably reduced amount of natural organic materials.

Proteinase K effectively removes the natural organic materials as part of Protocol B, which offers the advantage of taking less time than Protocol A (1 week for Protocol A vs. less than a half-day for B). Protocol A however is efficient in the tested water and less expensive; this protocol was thus selected and implemented for all samples during this PhD thesis program.

1.2 Separation from the mineral fraction

Reducing the organic fraction on its own is often insufficient to facilitate microplastic observation and analysis. The mineral fraction must also be efficiently removed. To do so, we have made use of the specific density of plastic polymers, which is less than the average specific density of mineral material (2.65 g.cm^{-3}) (Hidalgo-Ruz *et al.*, 2012). As mentioned in our review (Dris *et al.*, 2015), many previous works introduced NaCl for density separation. With a density of around 1.2 g.cm^{-3} however, NaCl does not include all plastic polymers. In fact, the plastic density ranges between 0.9 and 1.45 g.cm^{-3} , as presented in Chapter 1.

In this work, zinc chloride (ZnCl_2 , made available by Carlroth), which can attain a density above 1.6 g.cm^{-3} , was chosen. The solution was prepared by placing 700 g of ZnCl_2 crystals into 500 ml of water run through osmosis and filtration. For each prepared solution, the final density was verified by weighing. Regular weighing has revealed a density of 1.660 g.cm^{-3} ($\pm 0.060 \text{ g.cm}^{-3}$).

Following natural organic matter removal, the samples were placed in an oven to enhance their concentration, before being transferred into a separation funnel and adding ZnCl_2 . The solution was then stirred for 2 to 3 minutes. After a few hours (2 to 24 hours depending on sample type), the mineral particles sank and had to be eliminated. The supernatant was kept and vacuum filtered on glass fiber filters (GF/A Whatman filters, $1.6\text{-}\mu\text{m}$ mesh size).

2. QC/QA precautions

Many studies have reported that samples are often contaminated with fibrous microplastics, apparently stemming from textiles. To distinguish the contamination from the samples, a number of procedures therefore had to be carried out, namely:

- The samples were permanently covered with an aluminum foil in order to prevent airborne contamination;
- Only clean glass vessels were used, yet fibers and microplastics can very easily adhere to such vessels. All vessels were therefore heated to 500°C for 4 hours prior to use so as to eliminate any microplastic polymers still adhering to them. Moreover, the vessels were covered with aluminum foil immediately after retrieval from the oven.
- The glass fiber filters might have been contaminated even before their first use. In fact, a direct observation of filters from their box sometimes indicated fibers on them. Consequently, the filters were also heated to 500°C for 4 hours before filtration. An inspection of select filters after heating did not reveal any fibers or particles.
- Except for the nylon nets introduced, all use of plastic items was avoided. Cotton lab coats were worn during all laboratory procedures.

While contamination can be easily avoided during many steps, filtration is a more delicate process since the samples cannot be covered. It is important to pour the samples onto the filtration system before turning on the vacuum pump and then turning off the pump once the sample has passed through the filter. This step is performed to avoid any air filtration.

Blanks were performed and subjected to the same treatments as the samples (at 8 different times over the project duration). Between 0 and 3 fibers per blank filter were observed, which is negligible compared to the large number of particles observed on sample filters. In fact, in contrast with biota samples processed in other studies, the environmental samples derived in an urban context are very rich in fibers. The number of fibers in the samples is much greater than the potential contamination provided all the precautions cited above have been respected.

3. *Observation and counting of particles*

The filters were observed with a stereomicroscope (Leica MZ12) coupled to an image analysis software (HISTOLAB®) at a magnification of "x 16". Higher magnification was needed for some particles that could barely be identified (small particles, transparent fibers, etc.). In order to verify limited variability on the part of the operator, the same filter was observed by four different operators. The resultant variability was less than 5%.

3.1 *Counting of fibers*

Man-made fibers are either artificial (like rayon) or synthetic (plastic materials) (see discussion in Chapter 1). It was decided herein to assess the number of artificial fibers as well as the synthetic fibers even when their chemical structure is natural. Like with plastic polymers, these fibers contain many dyes and additives, some of which are intended to slow their degradation. In considering their potential environmental relevance and the fact that their sources and dynamics in freshwater are similar to those of synthetic fibers, all artificial fibers were thus included in the counting process. Moreover, it was impossible to visually distinguish between the different types of man-made fibers. This observation was conducted by ensuring the exclusion of all biological natural fibers. To achieve this, the following previously published criteria were used ((Hidalgo-Ruz *et al.*, 2012; Norén, 2007)):

- The fibers must remain of equal thickness throughout their entire length;
- The fibers must not be entirely straight, which would indicate a biological origin;
- No cellular or organic structures should be visible;
- Transparent fibers are to be examined at higher magnification to confirm their nature. Green fibers are also carefully observed since this color is very widespread on natural particles.

To avoid any overestimation, fibers of a highly uncertain type were not counted. The software (HISTOLAB®) allowed measuring the fiber length. As regards the observation method employed, the fibers shorter than 50 µm were hard to identify and therefore not taken into account. 50 µm was thus adopted as our lower limit of observation.

3.2 Counting of fragments and spheres

Plastic fragments and spheres were also counted. This effort was easier than counting fibers since the main error source, i.e. mineral particles, was removed during the density separation step. Great care was taken to avoid the overestimation of microplastics. Any particle of an uncertain type was ignored. All particles were measured with the software (larger size, smaller size, area and perimeter). Particle color and shape were also recorded.

4. *Chemical characterization*

Chemical characterization comes next in the plastic characterization process. Not only does chemical characterization help estimate the accuracy of the visual observations, but moreover polymer identification allows for a better interpretation regarding microplastics sources and dynamics. In general, macroplastics can be easily identified with the naked eye. However, to be certain of the polymer encountered, a Fourier transform infrared spectrometer, coupled to an attenuated total reflectance accessory, was used (FTIR-ATR). Due to the small size of microplastics, spectroscopic methods combined with microscopes are preferred for the characterization step. Both Raman and Fourier Transform InfraRed (FTIR) microspectroscopy have been tested.

4.1 *FTIR-ATR*

Macroplastics were analyzed using a Fourier transform infrared spectrometer coupled to an Attenuated Total Reflectance accessory (FTIR-ATR) made by PerkinElmer (spectrum BX). The wavenumber ranged between 4,000 and 1,000 cm^{-1} ; 4 scans were performed with a 4 cm^{-1} resolution. Plastic debris was identified by applying spectroscopy software to the spectrum and using a database containing spectra references of the various polymers (Sadtler ATR of Polymers, with 2,390 spectra). In this work, all the macroplastics encountered could be easily and quickly characterized.

4.2 *Raman microspectroscopy*

Raman microspectroscopy offers the capability of analyzing samples over a very small size range (down to the micrometer) and can be developed to simplify automation and therefore save time. Moreover, this method is non-destructive and does not require any additional sample preparation. The particles may be analyzed directly on the filter surface.

An optical microscope is used to detect the particle for analysis. This microscope will then focus the laser beam on the selected particle surface; the spectrum obtained can then be compared to a database.

Raman analysis was performed at the ICMPE (Paris-Est institute of Materials Chemistry). A Raman microspectroscope Horiba Jovin Yvon (Xplora) was employed; it was equipped with

two diode lasers, of 638 and 785 μm . The microscope was equipped with three different objective lenses (x 10, x 50 and x 100).

Since fibers are the predominant shape of microplastics, they were tested first and detected using the (x 10) objective lens before being analyzed with the other two magnifications. Both wavelengths were tested for all fibers.

Even though Raman microspectroscopy is often labeled a non-destructive method, the fibers are still destroyed by the excitation lasers. We had to systematically apply a 99% filter in order to limit the laser energy. During these analyses, the lasers were therefore operating at just 1% of their energy rating.

Raman spectroscopy was not conclusive in analyzing the fibers. For the n=60 fibers tested from different matrices, no interpretable spectra were obtained, except for one fiber of polyester in a washing machine effluent sample. Their identification was impossible even with optimization of the various parameters, including laser wavelength, acquisition time or laser intensity. A fluorescence phenomenon occurred and prevented collecting the Raman signal of polymers. This fluorescence is attributed to the organic material adsorbed on the fibers and additives, but most likely stemmed from the dyes incorporated into the polymers during their production.

4.3 FTIR microspectroscopy

Fourier Transform InfraRed (FTIR) microspectroscopy displays advantages similar to those of Raman microspectroscopy. However, the lower size limit of this analysis methodology is higher (5 μm). Three modes are available for FTIR microspectroscopy, i.e. ATR mode, reflection mode and transmission mode. The transmission mode was not tested in this work.

The ATR mode (attenuated total reflectance) was tested first; in this mode, the ATR crystal enters into contact with the sample. The top surface layers (a few micrometers thick) of the sample are excited with infrared light and the reflectance is calculated to obtain the spectrum.

An FTIR microspectroscope made by the Bruker corporation (Lumos) was used. The system has been entirely motorized, including the ATR crystal. While this system may be fully automated, it is not compatible with the ATR mode since the ATR crystal must be rinsed

between analyses to remove fibers that remain attached. In the case of a microplastics analysis, the automated ATR mode therefore may not be applied. Blanks must also be performed before each analysis due to the change in analyzed surface area based on particle shape and size. The measurements were conducted with a (x 8) objective lens. This method was very conclusive and effective for nearly all the analyzed particles, including fibers. Nonetheless, it is time-consuming. A wide range of databases were used to identify the spectra, including a database of fibers (both natural and man-made) as well as a database of plastic polymers.

The FTIR microspectroscope of the LDCM (Detection, Sensors and Measurements Laboratory), which is affiliated with the French Research Institute for Exploitation of the Sea (Ifremer), was employed for the reflection mode. It is an FTIR made by the Thermo Scientific corporation (i.e. the Nicolet Continuum model). As opposed to the two previous methods, according to which the analysis could be performed directly on the filter, this transmission requires transferring the microplastics to a reflecting surface. Fine tweezers were introduced to remove the fibers and fragments from filters and place them under the microscope. An objective of (x 10) was used to detect the targeted particles, and the analysis was carried out with the (x 32) lens. A signal blank was set to activate every 100 minutes. To some extent, this mode was less efficient than the ATR mode. In fact, not only was it more time-consuming due to the fact that analyses cannot be carried out directly on the filter, but moreover it did not systematically produce an exploitable signal. Efficiency was still acceptable as 80% of the particles were generating an identifiable signal. Due to access constraints, both FTIR modes were used herein.

4.4 Microplastic characterization

While the importance of the characterization step was clearly in our minds and we were also planning to implement it on all samples, for technical and financial reasons, we were unable to access a suitable characterization device for the first two years of the project. During last year, we finally gained access to the various devices presented above thanks to partners (ICMPE, LDCM Ifremer, Bruker). Nonetheless, this access was very limited and only a total of 10 days of analysis could be performed. Due to the time-consuming nature of these analyses, this short amount of time was definitely a constraint.

We therefore had to select the samples to be characterized by factoring in this constraint. Such a restriction also dictated the approach chosen. We actually decided to focus on certain compartments relative to their characterization. Moreover, for each compartment, we randomly selected the fibers or fragments to be analyzed. In this context, characterization was performed for the following particles:

- The air compartment as well as atmospheric fallout were characterized as a priority; this decision came at the expense of other compartmental sources. As an example, for WWTPs, previous works had provided an idea of the proportion of natural fibers in comparison to synthetic ones, yet our work is the first to investigate the atmospheric compartment. Consequently, it struck us as more essential to concentrate efforts on this compartment.
- Since freshwater environments lie at the center of this issue, both fibers and fragments were characterized within this compartment.

It is widely known to those who have previously worked with microplastics that the visually counted fibers are not always microplastics. In fact, a large proportion often consists of cotton fibers, either natural or artificial (rayon). In this manuscript, for each compartment, the total fiber concentrations will be indicated. The reader should keep in mind that references always pertain to a total number of fibers, including both natural and man-made (artificial and synthetic). Whenever subsamples of a compartment are characterized, we provide the proportion of each type of fiber, indicating the potential quantity of microplastics. We will also refer to previous studies during this work in order to estimate the proportion of microplastics that should be expected in non-characterized compartments.

While previous works have shown that visual counting causes an overestimation of fibers, they have also pointed to an underestimation for fragments (Song *et al.*, 2015). We consider that, in general and as opposed to fibers, no natural particle will be miscounted as a microplastic as long as we proceed carefully. We can however easily overlook some plastic particles. The characterization of fragments analyzed in this work only showed plastic polymers (except for one unidentified fragment) and was exclusively used to identify the predominant polymers.

Chapter 3: Estimation of macroplastic debris in urban rivers

“It seemed unbelievable, but I never found a clear spot. In the week it took to cross the subtropical high, no matter what time of day I looked, plastic debris was floating everywhere: bottles, bottle caps, wrappers, fragments”

Charles Moore, discovering the Pacific Garbage Patch

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This chapter is focused on macroplastic contamination and fluxes. Two approaches have been adopted.

The first one, performed in collaboration with the Paris Metropolitan Area's public sanitation authority (SIAAP), will be presented and examined at the beginning of this chapter; it has been intended to evaluate the quantity and quality of floating plastic debris flowing down the Seine River within the Paris Metropolitan Area. The floating debris, intercepted by a large regional network of debris-retention booms, was first analyzed before extrapolation to the total amount of plastics flowing over the entire section. These results provide a comprehensive evaluation of floating plastic debris at expanded spatial and temporal scales.

To draw a comparison, HCMC was considered for a second site study. Two canals were considered given that both were highly impacted by considerable human activity, including unauthorized garbage dumping. This work offers an assessment of macroplastic contamination for cities with two completely different waste management facilities.

A second approach was then carried out in order to theoretically approximate floating plastic debris. Similar to the approach employed by Jambeck et al. (2015) at the worldwide scale, based on waste quantities produced per capita, this protocol assesses the proportion of plastics in waste and a number of hypotheses related to waste littering, as well as the input from the Paris Metropolitan Area into the Seine River.

I. Assessment of floating macroplastics in the Seine River

This section is mainly based on an article we previously published in *Environmental Pollution* in 2014:

Gasperi, J., Dris, R., Bonin, T., Rocher, V., and Tassin, B. (2014). Assessment of floating plastic debris in surface water along the Seine River. Environ. Pollut. 195, 163–166.

1. Site description and sampling approach

To avoid any visible pollution on the Seine River, the SIAAP has deployed a network of floating debris-retention booms since 1990. This network is composed of 26 booms on the Seine and Marne Rivers. On the Seine, booms are distributed along a 77 km stretch. Each boom is cleared once a week using cleaner boats equipped with a conveyor belt, a coarse shredder and several garbage dumpsters. Based on 6 years of monitoring (2008-2013), the average mass load of extracted floating debris averaged 1,937 tons per year (estimated range between 1,590 and 3,790 tons) (SIAAP database).

Test campaigns were conducted from April to July 2014: Seine River flow varied between 80 and 290 m³.s⁻¹. A total of 10 booms were considered (Figure 16). For boom no. 3, two duplicate campaigns were carried out. After mechanical homogenization of the garbage dumpster, approximately 10 kg of crushed debris were collected for each boom using 5 sub-samples. The collection method carried out by the boats didn't allow the sampling before the passage of the debris through the crusher. The debris were sorted by type and then classified into 3 categories: vegetal, plastic, and other (including, for instance, glass and aluminum cans). For the plastic debris category, all items were dried, weighed and then characterized by ATR-FTIR spectroscopy (Chapter 2).

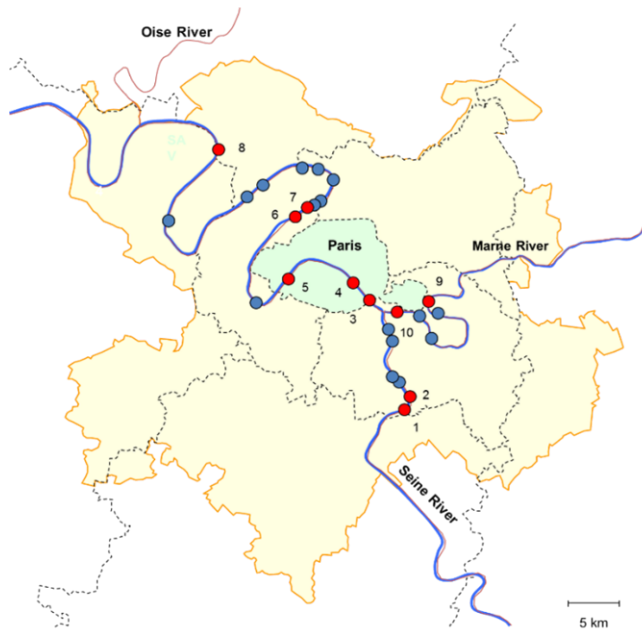


Figure 16: Paris area network of floating booms (studied booms shown in red), plus photograph of a floating boom and floating debris collected

2. *Percentage of plastic debris and litter composition*

Regardless of the boom considered, vegetal debris was predominant, representing between 92.0% and 99.1% of total floating debris by weight. Natural and manufactured wood and all sorts of plants were found. The "other" floating debris accounted for 0.0% to 6.8% of the totals depending on the particular sample. The mass percentage of plastic debris ranged between 0.9% and 6.3%, with an average value of 2.1%.

A significant proportion of the collected plastics has consisted of food wrappers/containers, plastic cutlery and plastic bottles. Relatively few plastic bags were observed. The predominance of food consumption-related plastics is primarily due to recreational activities, with direct or indirect dumping into the Seine, in addition to runoff and CSO discharges.

The composition litter is similar to that determined in the Thames River by Morritt *et al.* (2013), with the exception that in our study, no tobacco packaging/wrappers or sanitary towel components were found. These differences may be related to: i) the methodological approaches and devices deployed for floating and submerged items; ii) the differing types of hydraulic and dynamic behavior between study sites (river vs. estuary area); and iii) likely differences in waste management practices.

Rech *et al.* (2014) provided information on the composition of plastic litter for 4 Chilean rivers. These authors indicated that persistently buoyant items, especially plastics, were the most abundant litter components, yet they did not offer any more detailed information on the types of plastic found. Due to a lack of gray literature data, only a coarse comparison could be drawn in 2013 with a local organization's results (Mal de Seine, <http://maldeseine.free.fr/OSPAR.html>) about 100 km downstream of Paris. In adapting the Guideline for Monitoring Marine Litter on Beaches in the OSPAR Maritime Area and collecting all plastic debris along a 117 m stretch of riverbank, a total of 17,000 items were collected, including 5,274 polystyrene objects, 2,981 cotton buds, 1,660 caps, 1,136 food containers and 3,988 confectionery packages. Sanitary products, including towels and back strips, were also observed (88 items).

Except for boom no. 6, the percentage of plastic debris was quite homogenous across all sites, varying only from 0.9% to 2.7% (Figure 17). For boom no. 3, the mass percentage variability

was estimated at $1.5\% \pm 0.5\%$ ($n = 4$). From a global perspective, no clear difference in plastic loads could be identified between the upstream and downstream sections of the Seine River. The high percentage of plastic for boom no. 6 is consistent with its immediate proximity to the largest CSO outfall within the Paris metropolitan area (Gasperi *et al.*, 2012) and with a CSO discharge of about $100,000 \text{ m}^3$ that occurred prior to sampling.

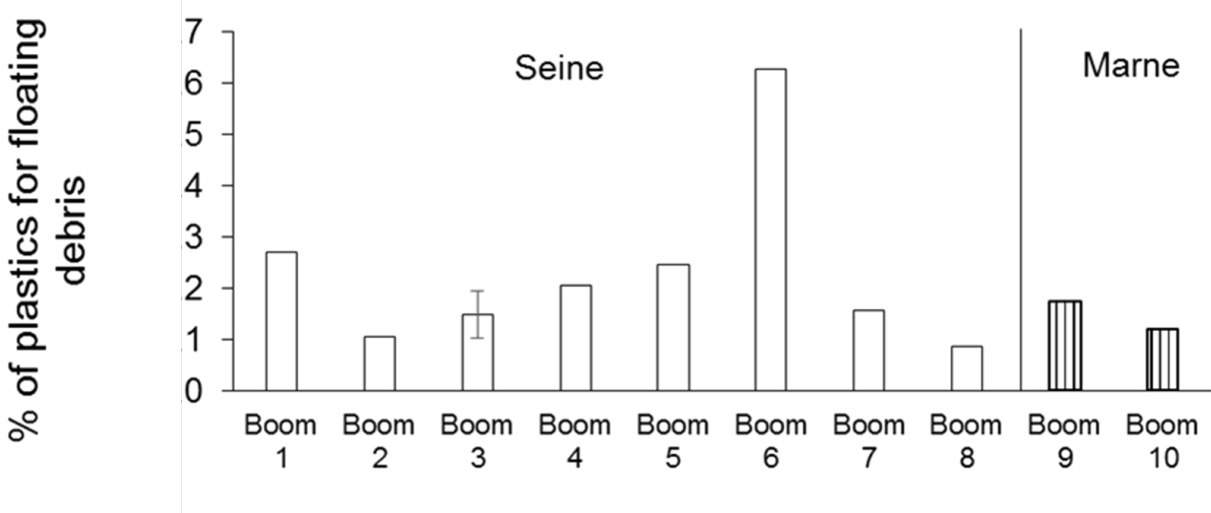


Figure 17: Dry mass percentage of plastic debris, in comparison to the total floating debris (%). For boom no. 3, the average value is presented with variability.

3. Nature of the plastic debris

The nature of floating plastic debris is depicted in figure 18. Most plastic items intercepted by booms contain PP (35.2% ± 21.6%, average value ± standard deviation) or PE (LD+HD) (26.0% ± 14.6%), and to a lesser extent PET (20.7% ± 20.1%). The remaining resin categories account for 10.8% ± 12.3% in PS and 7.4% ± 11.4% in O (PA, Acrylic, POM, PC).

The plastic masses varied significantly from one boom to the next; this finding is mainly correlated with the methodological approach adopted and with the random distribution of plastic items. Interestingly, the resin pattern observed for plastic debris is roughly similar to that of plastic production for packaging uses (Chapter 1). Packaging applications actually account for the largest single sector within the plastics industry (39.4%).

The absence of PVC items intercepted by these booms may be explained in large part by both their uses and the probable routes leading to river discharge. PVC in fact is mainly used in the building and construction sector; it can reasonably be assumed however that few routes are available for construction products to end up in rivers. PVC also has a higher density than other plastics, thus making it absent on the surface.

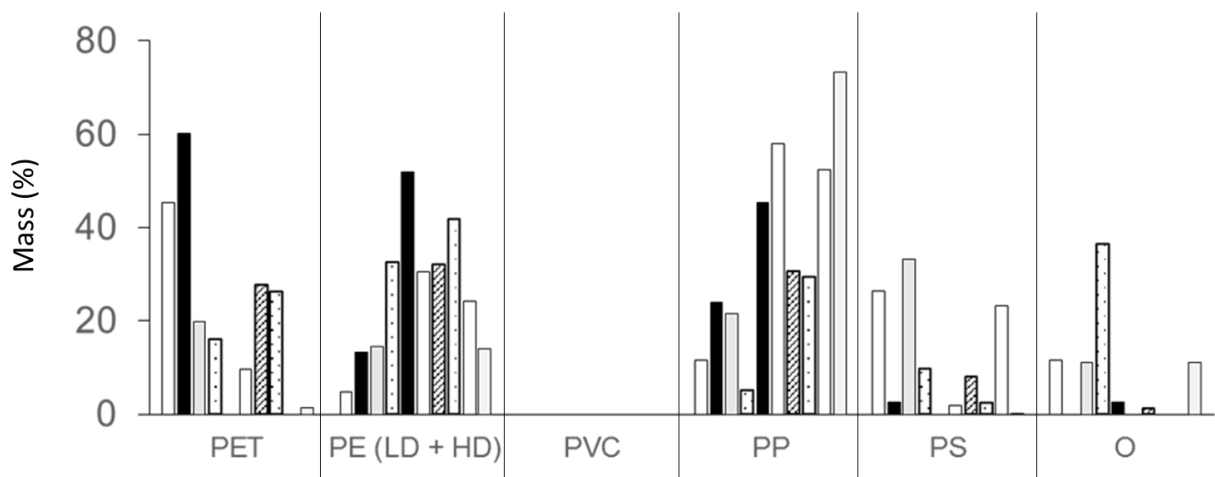


Figure 18: Type of floating plastic debris (in %) (From left to right: boom 1-10).

4. Evaluation of plastic debris mass loads conveyed by the Seine River

The amount of floating plastic has been estimated based on three hypotheses, corresponding to the minimum, median and maximum mass percentages of plastic found in the booms (Table 4). At the annual scale and based on the median hypothesis, between 33 and 54 tons (mean value: 40 tons) of floating plastic debris are intercepted annually by the SIAAP boom network on both rivers. This debris would be deposited along riverbanks or floors and/or transferred into the English Channel. Although the plastic targeted in this study differs from that investigated by Lechner *et al.* (2014), this 40 ton figure is much lower than the plastic being conveyed to the Black Sea by the Danube, i.e. 1,500 tons a year (let's keep in mind however that the populations considered in both studies differ significantly, i.e. roughly 12 million for the Seine River Basin vs. 100 million for the Danube).

Table 4: Metric Tons of floating plastic debris conveyed by the Seine River (* corresponding to the minimum, maximum and median plastic mass hypothesis).

| | | % floating plastic debris hypotheses* | | |
|-------------|-----------------------|---------------------------------------|------|------|
| | Total floating debris | 0.9% | 2.1% | 6.3% |
| 2007 | 1,818 | 16 | 38 | 115 |
| 2008 | 2,157 | 19 | 45 | 136 |
| 2009 | 1,591 | 14 | 33 | 100 |
| 2010 | 1,636 | 15 | 34 | 103 |
| 2011 | 1,706 | 15 | 36 | 108 |
| 2012 | 1,969 | 18 | 41 | 124 |
| 2013 | 2,564 | 23 | 54 | 162 |
| Mean | 1,920 | 17 | 40 | 121 |

Given the local Paris Basin population (12 million) and considering the mean values from these three hypotheses, the mass of floating plastic debris per capita per year has been evaluated at between 1.4 and 10.1 g. In comparison, the input per capita over the Danube Basin might reach approximately 20 g a year. This rough comparison supports the finding of a large relative share of floating plastic debris among total plastic input.

An underestimation of floating plastic debris is also possible since the boom capture efficiency remains unknown. Both the high level of barge traffic and river meanderings could sweep floating debris to the riverbank, enhancing debris interception by booms, and therefore severely limiting this bias. Plastic debris "leaks" can nevertheless occur along riverbanks. The presence of plastic debris had already been observed along the Seine banks. More specifically, the *GIP Seine-Aval* (a public interest consortium) identified accumulation zones on the banks along the downstream part of the Seine (from the river's estuary nearly to the city of Rouen). It is plausible that similar accumulation zones are also present upstream, which would require further investigation (*GIP Seine-Aval, 2015*).

The effect of high flow and flooding periods Seine needs to be determined as well. In fact, the assumption could be made that this deposited debris is remobilized during flooding. Runoff might also be a strong contributor of the plastic debris found in the Seine, along with direct dumping, both of which warrant further consideration. For instance, at the Ivry-Masséna stormwater storage tunnel facility, a very large amount of accumulated plastic debris has been observed, with this debris mainly consisting of bottles. Each year, the tunnel is shut down for two weeks in order to retrieve all the plastic debris clogging the tunnel.



Figure 19: Plastic debris on the banks of the Seine River. The two top pictures are taken from the site of the association Berges-Saines (<http://www.berges-saines.fr/francais/berges-saines/>) while the two bottom pictures were taken from the site of the association S.O.S mal de Seine (<http://maldeseine.free.fr/OSPAR.html>).

The above estimation was based on what was trapped by the floating booms. These booms covered just a small fraction of the water section. Based on the average-sized boom and the average water velocity on the Seine, it could be estimated that an average water flow of $8.6 \text{ m}^3 \cdot \text{s}^{-1}$ passes through each boom annually. It can therefore be estimated that if all Seine River water in the Paris Metropolitan Area were to pass through the booms (i.e. $350 \text{ m}^3 \cdot \text{s}^{-1}$), an average of 1,000 metric tons could be collected.

A different hypothesis can be used for this estimation by considering the dimensions of the Seine River water section in comparison to those of the floating booms. On average, the Seine River is 20 times wider than a boom, while its depth is 10 times greater than that collected by the booms. According to this approach, it was estimated that up to 5,400 metric tons of plastic could flow along the Seine River annually.

II. Assessment of floating macroplastics in Ho Chi Minh City

1. Site description and sampling approach

To study macroplastics in HCMC, plastic debris larger than 5 mm were sampled in the Nhieu Loc - Thi Nghe Canal (Figure 20). On this canal, floating garbage is collected manually by a company. Workers collect garbage on boats carrying containers to accommodate the floating waste. This step requires a net with a large mesh size (1.5 - 2 cm) towed on each side of the boat and collects inaccessible waste using a sort of landing net (Figure 21).

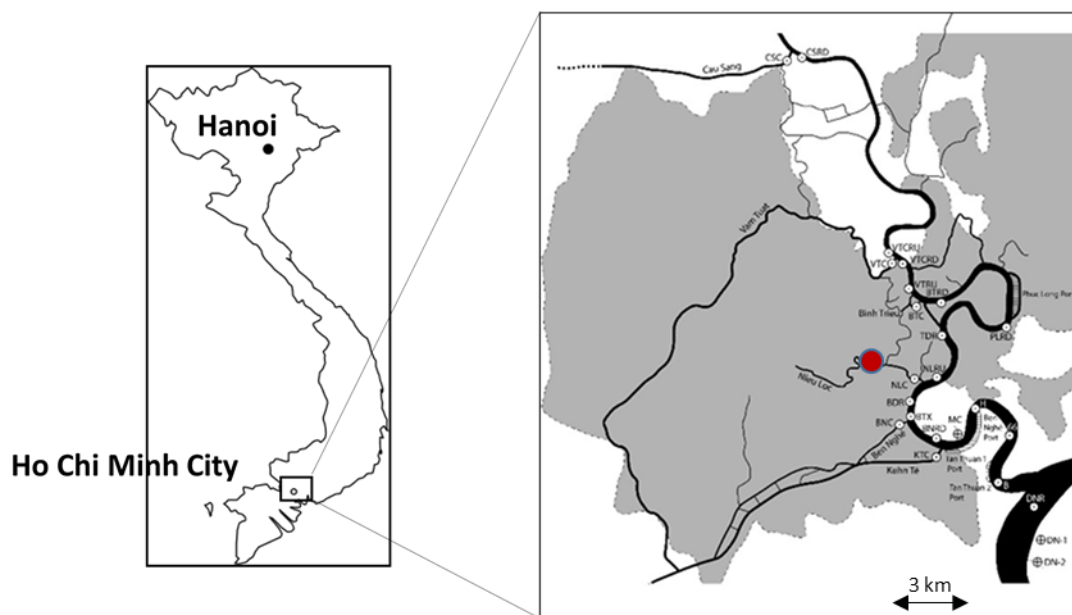


Figure 20: Location of the sampling site.



Figure 21: Garbage collection on Nhieu Loc - Thi Nghe.

Garbage is collected every day on Nhieu Loc. Observation campaigns conducted aboard the boats have assessed the efficiency of this collection process. Floating waste is thoroughly collected and therefore representative of canal contamination. Moreover, data on the canal basin population density are available. The collection company has estimated that approximately 10 - 12 metric tons of garbage are collected every day on Nhieu Loc.

On the Nhieu Loc - Thi Nghe Canal, the various sections where floating garbage is collected have been identified, and a range of containers are used for each section. Samples are extracted from defined sections of this canal. Two campaigns were conducted here in April 2016 (on the 12th and 21st). A total of 5 garbage samples from the containers were collected: two from a slum area on a small tributary of the canal, and the other three from the canal itself, one upstream, one downstream and one from an undetermined portion (Figure 22).

For each sample, 6 to 7 kilograms of garbage were taken from the container before being returned to the laboratory. Since this garbage may be hazardous, it was stored in a remote place before handling. The collected garbage was sorted in the laboratory into the following categories: organic refuse, plastic waste, and other (aluminum cans, paper, glass, cloth, etc.). The plastics were then separated into 3 groups: plastic bags, polystyrene (PS), and other (Figure 22). These various types of garbage were then weighed while still wet in order to derive the mass percentage of each category, knowing that our estimations are based on the total wet weight given by the collection company. Despite its interest as a data element, the dry weight could not be considered due to a lack of adequate equipment to dry the garbage and the potential hazard of the samples.



Figure 22: Sort out and field pictures during collection.

2. Characterization of floating plastic debris

On the Nhieu Loc - Thi Nghe Canal, as the two campaigns were being conducted (12th April and 21st April 2016) and with several samples being taken during each campaign, over 21 kg of garbage was sampled in all (Table 5). Within this quantity of extracted garbage, organic debris accounted for 67% of the weight and was mainly composed of water jacinth and coconut shells. Other debris, namely aluminum cans, glass bottles, cigarette packs, medication tablets, cloth and other non-plastic items accounted for just 7% by mass. The plastic waste mass ranged from 11.5% to 43.3% of the total garbage weight, with a mean of 26.3%.

Table 5: Results of garbage sort out in Nhieu Loc – Thi Nghe canal.

| | Sample | Organic | Plastics | Others | Total |
|----------------------|-------------------------|---------|----------|--------|--------|
| Garbage weight (g) | <i>Slum area 12.04</i> | 4,088 | 530 | 0 | 4,618 |
| | <i>Slum area 21.04</i> | 3,380 | 1,078 | 400 | 4,858 |
| | <i>Upstream 12.04</i> | 2,182 | 1,844 | 232 | 4,258 |
| | <i>Downstream 12.04</i> | 1,954 | 1,777 | 687 | 4,418 |
| | <i>Canal 21.04</i> | 2,629 | 363 | 126 | 3,118 |
| | <i>Mean</i> | 14,233 | 5,592 | 1,445 | 21,270 |
| Mass % / total waste | <i>Slum area 12.04</i> | 89 | 11 | 0 | - |
| | <i>Slum area 21.04</i> | 70 | 22 | 8 | - |
| | <i>Upstream 12.04</i> | 51 | 43 | 5 | - |
| | <i>Downstream 12.04</i> | 44 | 40 | 16 | - |
| | <i>Canal 21.04</i> | 84 | 12 | 4 | - |
| | <i>Mean</i> | 67 | 26 | 7 | - |

Plastic bags made up 37% of total plastic waste and 9% of total garbage by weight. Polystyrene was found from 9 to 22% of plastic weight and 2 to 7% of total waste weight. It was found as containers and food packaging. Other plastic waste was composed of plastic bottles, food wrappings, drinking recipients and plastic cutlery. This category constituted nearly half the weight of plastic debris and around 11% of total garbage weight (Table 6).



Figure 23: Various plastics collected on the canals.

A number of differences can be observed in garbage composition between the 2 campaigns as well as from one sector to the next. These differences can be explained in part by the fact that the samples were not collected at the same time of day for both campaigns. In fact, many people walk along the canal in the evening and throw litter into it. In the morning, many food packaging items from takeaway meals consumed the previous evening are found on the canal and collected by the campaign crew. The first campaign took place in the morning while the second was conducted during the afternoon. Regarding plastic waste, PS was found in a larger proportion in the first campaign than in the second, thus confirming the hypothesis of takeaway packaging being discarded during the evening. Regarding the plastic waste composition from the various sectors, let's note that the only significant difference lies in the amount of plastic bags found upstream on the canal, as this amount is smaller than in any other section, owing perhaps to the dynamics of the canal when flowing into the Saigon River.

Table 6: Results of plastic waste sort out in Nhieu Loc - Thi Nghe canal.

| | Sample | PS | Bags | Others | Total |
|------------------------|--------------------------------|------------|--------------|--------------|--------------|
| Garbage weight (g) | <i>Slum area 12.04</i> | 73 | 192 | 65 | 330 |
| | <i>Slum area 21.04</i> | 91 | 391 | 479 | 961 |
| | <i>Upstream 12.04</i> | 290 | 424 | 1,040 | 1,754 |
| | <i>Downstream 12.04</i> | 216 | 728 | 675 | 1,619 |
| | <i>Canal 21.04</i> | 48 | 132 | 154 | 334 |
| | <i>Mean</i> | 718 | 1,867 | 2,413 | 4,998 |
| Mass % / total waste | <i>Slum area 12.04</i> | 2 | 4 | 1 | 7 |
| | <i>Slum area 21.04</i> | 2 | 8 | 10 | 20 |
| | <i>Upstream 12.04</i> | 7 | 10 | 24 | 41 |
| | <i>Downstream 12.04</i> | 5 | 16 | 15 | 37 |
| | <i>Canal 21.04</i> | 2 | 4 | 5 | 11 |
| | <i>Mean</i> | 3 | 9 | 11 | 23 |
| Mass % / total plastic | <i>Slum area 12.04</i> | 22 | 58 | 20 | - |
| | <i>Slum area 21.04</i> | 9 | 41 | 50 | - |
| | <i>Upstream 12.04</i> | 17 | 24 | 59 | - |
| | <i>Downstream 12.04</i> | 13 | 45 | 42 | - |
| | <i>Canal 21.04</i> | 14 | 40 | 46 | - |
| | <i>Mean</i> | 14 | 37 | 48 | - |

For the Nhieu Loc -Thi Nghe Canal, since data on its basin population density are available, the plastic leakage weight per capita has been estimated according to several hypotheses. The first hypothesis concerned the garbage weight collected per day. The two amounts of 10 and 12 metric tons were considered (data provided by the collection company). The second hypothesis assumed the percentage of garbage captured by the collecting team, with values of 50%, 80% and 100%, since collection on this canal seemed to be very thorough. Different percentages of plastic relative to total garbage weight, i.e. minimum (11.5%), maximum (43.3%) and mean (26.3%), were also selected. Moreover, two population densities were tested, one stemming from a 2012 World Bank report (1.2 million inhabitants) the other from a 2014 article on the canal redesign project (60,000 population per km over a length of 8.7 km, amounting to 522,000 inhabitants). After taking into account these hypotheses, plastic leakage on the NL basin was found to lie between 0.96 and 19.91 g per person per day, spanning the minimum and maximum hypotheses. The median was calculated at a daily 4.43 g per capita, which amounts to roughly 1.6 kg per capita per year.

This figure is high compared to the 2.3 g per capita per year recorded for the Seine River. Leakage was found to be some 700 times greater in HCMC than in Paris. According to witness accounts on the canal during these campaigns, such an estimate seems to be adequate.

From the estimation carried out by Jambeck *et al.* (2015), a coastal population of approximately 60 million in Vietnam produces between 280,000 and 730,000 metric tons of marine plastic debris, i.e. the equivalent of between 4.6 and 12.5 kg per capita per year, which slightly exceeds the field estimation. This slight difference may be related to a field study underestimation. In this case, the contracted plastic collection has been considered as efficient. The uncollected fraction might be higher than expected. Jambeck's approach could have also overestimated the inadequately managed waste.

According to this same article, it was estimated that the world's coastal population (6.3 billion) releases between 4.8 and 12.7 million metric tons into the oceans annually, which corresponds to a release rate of between 0.7 and 2 kg per capita per year.

III. Theoretical estimation of the plastic flowing from the Paris agglomeration into the freshwater

In relying on Jambeck's methodology, this part of the chapter will seek to theoretically estimate the amount of plastics discharged into freshwater. The following paper was used for guidance:

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Plastic waste inputs from land into the ocean. Science 347, 768–771.

In Jambeck's study, the plastic mass flowing from coastal cities into the oceans has been estimated. In this section, the Jambeck approach will be reproduced for application to the Paris Metropolitan Area. Moreover, the plastic masses discharged from the Paris Region (Ile-de-France) into the Seine River have been approximated.

1. Understanding the Jambeck's paper methodology

In Jambeck's paper, it was estimated that from the 192 coastal countries, between 4.8 and 12.7 million metric tons are discharged into the oceans. To derive this estimation, a number of hypotheses had to be adopted. First, only the population living a distance of less than 50 km from the coast was considered. The paper then estimated the amounts of waste produced by this population and hypothesized on the fraction of this waste that gets mismanaged. The proportion of plastic materials among this waste also had to be approximated.

France is among the 192 countries considered in this study (Table 7). France's coastal population is easily known, thanks in large part to INSEE Office data. This information can thus be considered as precise. The waste generation rate is also a known value, as provided by EUROSTAT (Statistical Office of the European Union - <http://ec.europa.eu/eurostat/>).

Other values used in the article are less accurate and depend more heavily on rough estimations. The proportion of plastic in the waste stream is an estimation provided by the World Bank (<http://www.worldbank.org/>) although very little information is available on how this figure is approximated; it was generated based on questionnaires for each country.

The proportion of inadequately disposed waste corresponds to waste not formally managed and includes disposal in dumps and open uncontrolled landfills where the waste cannot be fully contained. This value depends on the country's economic performance as well as the waste management strategy employed. While it seems obvious that this value should be very low for France, the estimation has not been fully substantiated.

Littered waste is very hard to estimate because it corresponds to the fraction that remains inaccessible. Due to this difficulty, the same value of 2% was used for all countries; it was extracted from a report estimating the littered waste (i.e. National Visible Litter Survey and Litter Cost Study, MSWCONSULTANTS, 2009). The latter article used numerical values (waste quantity) while Jambeck's article only used mass measurements. Moreover, the littered waste estimation carried out in one study is based solely on the situation in the United States; this estimation therefore is very rough and its accuracy is impossible to evaluate.

Mismanaged waste was defined as material that is either littered or inadequately managed. It was then considered that between 15% and 40% of mismanaged plastic reaches the oceans. This value was determined from a report on water quality in the San Francisco Bay (Preliminary Baseline Trash Generation Rates for San Francisco Bay Area, BASMAA, 2009). This rough estimation therefore is highly questionable.

Table 7: Data used in the article of Jambeck et al., 2015 in order to estimate the mismanaged plastic in France.

| Type | Value | Reliability |
|---|-------------------------|-------------|
| Country | France | - |
| Economic Status | High Income Country | - |
| Coastal population | 17,287,280 | X |
| Waste generation rate (kg.inhabitant ⁻¹ .day ⁻¹) | 1.92 (kg) | X |
| Plastic in waste stream | 10% | X |
| Inadequately disposed waste | 3.68x10 ⁻⁹ % | X |
| Littered waste | 2% | X |
| Waste generation (day ⁻¹) | 33,191,587 (Kg) | - |
| Plastic waste generation (day ⁻¹) | 3,302,562 (Kg) | - |
| Inadequately managed plastic waste (day ⁻¹) | 0.0001 Kg | - |
| Plastic waste littered (kg.day ⁻¹) | 66,051 (Kg) | - |
| Mismanaged plastic waste (kg.person ⁻¹ .day ⁻¹) | 0.004 (Kg) | - |
| Mismanaged plastic waste in 2010 (metric tons) | 24,109 | - |
| Mismanaged plastic waste in 2015 (metric tons) | 34,671 | - |

X: Accurate estimation – X: Rough estimation

2. *Adapting the data to the case of the Paris agglomeration*

In the first section, the exact approach carried out by Jambeck *et al.* was reproduced for the case of Ile-de-France (the administrative region including the Paris Metropolitan Area). Similarly to what was estimated from the coasts to the oceans, it was considered here that 15% to 40% of mismanaged waste within the region ends up in freshwater.

The INSEE Office estimates the number of inhabitants in the Ile-de-France region at 12 million and the total amount of waste produced annually per capita at 482.88 kg. According to this approximation, it could be estimated that between 1,722 and 4,594 metric tons of plastic are introduced into the Seine River by the Ile-de-France region (Table 8).

Other estimations can be derived by using different techniques to approximate the levels of waste produced per capita. Data have been provided by SYCTOM (Metropolitan Household Waste Agency), which collects and treats waste throughout the Paris Metropolitan Area. As part of the SYCTOM data, it appears that each inhabitant produces 407 kg annually, a figure in close agreement with the INSEE numbers. These data also indicate that between 5% and 15% of the waste are plastic. Under this new hypothesis, it was approximated that a plastic mass of between 750 and 5,100 metric tons reaches the Seine River every year.

Table 8: Estimation of the plastic theoretically entering the Seine River by using the same data used by Jambeck et al., 2015.

| Type | Value |
|---|-------------------------|
| Region | Ile-de-France |
| Population | 11,952,061 |
| Waste generation rate (inhabitant-1.day-1) | 1.32 (Kg) |
| Plastic in waste stream | 10% |
| Inadequately disposed waste | 3.68x10 ⁻⁹ % |
| Littered waste | 2% |
| Waste generation (day-1) | 15,811,921 (Kg) |
| Plastic waste generation (day-1) | 1,573,286 (Kg) |
| Inadequately managed plastic waste (day-1) | 0.0006 Kg |
| Plastic waste littered (day-1) | 1,587 (Kg) |
| Mismanaged plastic waste | 11,484,990 (Kg) |
| Plastics into the Seine River - 15% of mismanaged plastic (metric tons) | 1,722 |
| Plastics into the Seine River - 40% of mismanaged plastic (metric tons) | 4,594 |

By considering the theoretical estimations in comparison to the estimation based on the field study, results are surprisingly close even if the approaches are completely different (Table 9). We can, in general, estimate that the amount of plastics flowing in the Seine River in the Paris Agglomeration is between 750 and 5,400 metric tons.

Table 9: The estimation of the annual masses of plastic flowing in the Seine River based on different approaches and hypothesis.

| | Minimum estimation | Maximum estimation |
|--|---------------------------|---------------------------|
| | (metric tons) | (metric tons) |
| Data of INSEE + Jambeck's approach | 1,722 | 4,594 |
| Data of SYCTOM + Jambeck's approach | 750 | 5,100 |
| Estimation based on the extrapolations of the field study | 1,000 | 5,400 |

IV. Conclusions

By investigating floating debris at a large regional scale in deploying a boom network, this study is one of the first to deliver reliable information on the quantity and quality of floating plastic debris conveyed by rivers. Plastic debris represents between 0.9% and 6.3% of total debris by weight. A significant proportion of these plastics consists of food wrappers / containers and plastic cutlery most likely associated with recreational activities, with a high probability of direct or indirect dumping into the Seine River. Most plastic items are made of PP, PE and, to a lesser extent, PET. According to the median hypothesis assumed, between 33 and 54 tons of plastic are intercepted annually by the booms, thus confirming that land-based sources are responsible for the majority of these inputs. At an annual scale, between 1,000 and 4,500 metric tons would be conveyed by the Seine River if these results were extrapolated to the complete section.

A Saigon River canal in HCMC has also been considered. A substantial mass percentage of plastic was indeed found, although it consisted of very light polymers. Plastic bags and polystyrene are thus a very significant part of overall canal pollution.

To compare our experimental results, a theoretical approach was adopted in addition to the field studies. The plastics input into the Seine River would amount to between 750 and 5,100 metric tons a year, a finding consistent with the field study approximation (1,000-5,400 metric tons).

By coupling the data collected with the number of inhabitants, the plastic leakage per capita into the aquatic environment could be estimated. Over one year, leakage into the Seine was approximated at between 0.06 and 0.45 kg of plastic per capita, depending on the estimation method, while it amounted to 1.6 kg per capita into the NL canal. The average annual input of plastic for the coastal population worldwide equals between 0.7 and 2 kg per capita. Different results obtained using different methodologies would therefore seem consistent.

Table 10: estimated amounts of plastic leaked per inhabitant per year into the aquatic environments.

| Estimated flux | Estimation method | Total per year | Per inhabitant per year (kg) |
|--|-----------------------------------|-----------------------|-------------------------------------|
| From – To | | (metric tons) | |
| Paris agglomeration – Seine River | Collected by the booms | 33 – 54 | 0.001 – 0.001 |
| Paris agglomeration – Seine River | Extrapolated to the whole section | 1,000 – 5,400 | 0.09 – 0.45 |
| Paris agglomeration – Seine River | Theoretical approach | 750 – 5,100 | 0.06 – 0.42 |
| Nhieu Loc canal basin inhabitants – Nhieu Loc canal | Collected by the cleaning company | 1,900 | 1.6 |
| French coastal population – Marine environment | Jambeck's estimation | 5,200 – 15,600 | 0.3 – 0.9 |
| Vietnamese coastal population – Marine environment | Jambeck's estimation | 280,000 – 730,000 | 4.6 – 12.5 |
| Worlds coastal population – Marine environments | Jambeck's estimation | 4.8 – 12.7 million | 0.7 – 2 |

Such data could contribute to a global evaluation of plastic inputs conveyed by rivers and released into the oceans. The correlations between plastic loads and certain river basin features (i.e. population, density, land use, waste management practices) must be further investigated. The amount of plastic debris per capita per year presented above may provide an insightful measure. These data might also help with the implementation of new more stringent regulations regarding plastic litter, in the aim of drastically reducing ocean plastic pollution. Further work is needed in various locations and countries in order to provide more accurate results. The pathways and routes relevant to plastic debris remain unknown; more specifically, the role of floods in plastic leakage must be determined.

Chapter 4: Sources of microplastics in an urban area



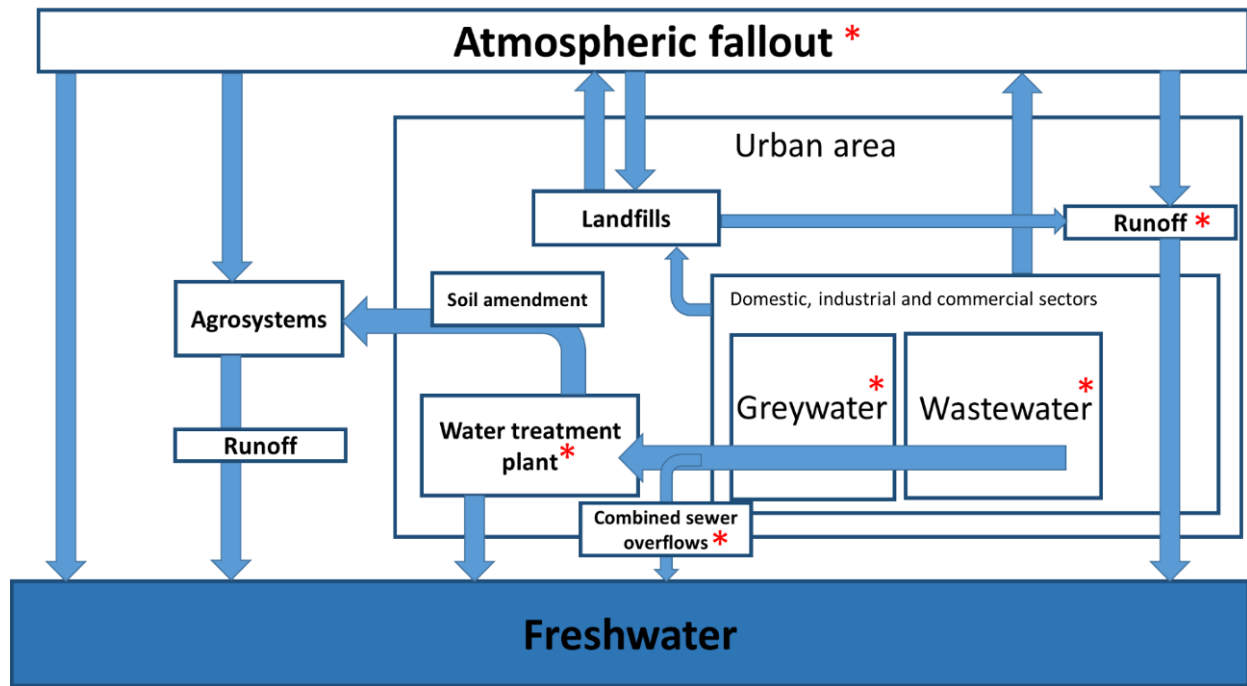
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This chapter will present various urban compartments. The air compartment will be considered in the first section, by means of investigating indoor concentrations, indoor deposition rates and fiber concentrations in settled dust collected from vacuum cleaner bags. At the same time, outdoor concentrations were also investigated, as was the potential of the atmospheric compartment to serve as a source of fibers, including microplastics, for the aquatic compartment. Consequently, atmospheric fallout was studied as well.

The second section will explore contamination in various urban waters (Figure 24):

- runoff harvesting/collecting the pollutants (including fibers and plastic fibers) that accumulate on urban surfaces during dry weather periods;
- greywater (washing machine effluent and floor washing water), to allow assessing the role of household activities as a source of microplastics and fibers;
- wastewater, treated outflow at two different WWTPs;
- combined sewer overflows (CSOs) containing both wastewater and urban runoff.



* Compartments studied in this chapter

Figure 24: The cycle of plastic pollution in the city with an indication of the studied compartments.

I. Air compartment

1. Indoor environment and outdoor concentrations

1.1 Sampling approach

Air was sampled in all four seasons during the year 2015. Three different indoor sites were selected: two private apartments (A and B) and an office. Outdoor air was sampled on the office building roof.

All sampling sites were located about 10 km from the Paris city center (Figure 25). Two adults and one child were living in each apartment (48°48'15.3"N, 2°27'53.7"E: Apartment A, 48°48'20.2"N, 2°24'48.9"E: Apartment B). Sampling was performed in the living room. The office and outdoor sampling sites were located at the University of Paris-Est-Créteil (48°47'17.8"N, 2°26'36.2"E). During sampling, the office was occupied by three employees.

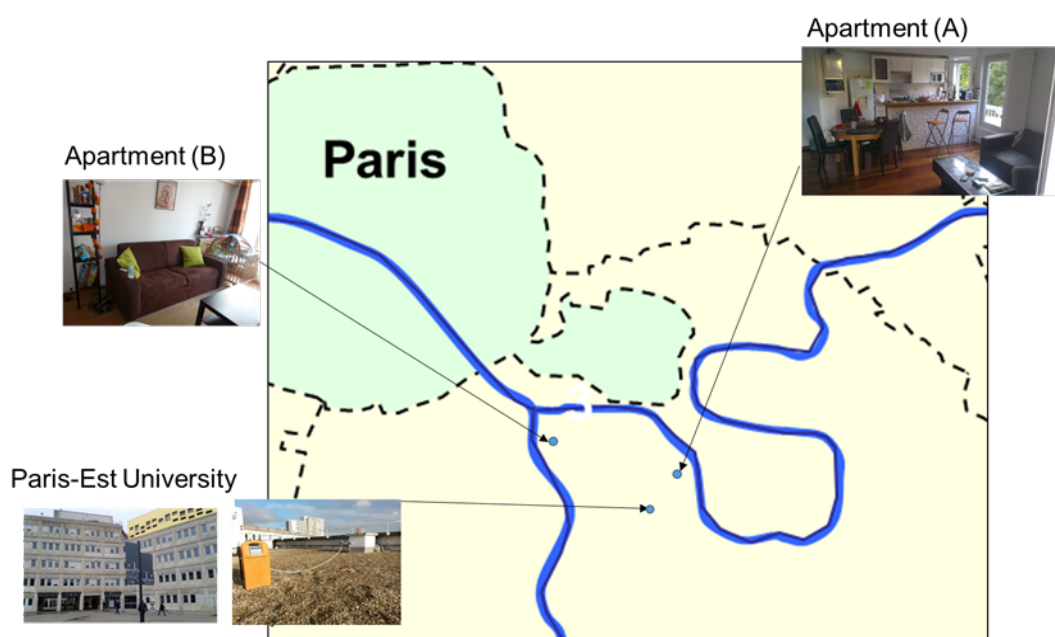


Figure 25: Location of the monitored sites.

A pump (stand-alone sampling pump GH300, Deltanova, France) was used to sample at 8 L.min⁻¹ of indoor air on quartz fiber GF/A Whatman filters (1.6 µm, 47 mm). The sampling steps were carried out at a 120-cm height for periods ranging between 4 and 7 hours, i.e. a volume between 2 and 5 m³ depending on the occupancy: partially (50%) in the morning before the

occupants left home and partially (50%) in the afternoon once they had returned, in order to sample the air only during their presence. The office site was continuously sampled during actual office hours. This same method was employed for outdoor air, yet with higher volumes (5 - 20 m³) being sampled. A triplicate was carried out per season for each of the indoor and outdoor sites, and the number of fibers per cubic meter was estimated.

A passive sampling of dust fall was conducted in order to estimate the fiber deposition rate. Quartz fiber GF/A Whatman filters (1.6 µm, 47 mm) were exposed once per season at each apartment (A and B) as well as at the office. Sampling was performed in the living room at a height of 120 cm. The exposure time varied between 4 and 15 days. The deposition rate was normalized and expressed as a number of fibers per square meter per day.

Three vacuum cleaner bag samples were also extracted, twice in Apartment A (winter and autumn) and once in Apartment B (winter). The samples were directly taken from the vacuum cleaners that study participants use in their daily life. To facilitate the subsequent sample treatment steps, it was necessary to pass the vacuum cleaner bag contents through a 2.5-mm meshed sieve. The retained fraction (> 2.5 mm) was visually inspected to determine whether it contained plastics. Since such was never the case, this fraction was systematically discarded. A 5.5-mg mass was introduced in a separation funnel with 50 ml of ZnCl₂ (1.6 g.cm⁻³) for the density separation step. Preliminary tests indicated a very high number of fibers. For this count to be feasible, only a subsample of a small volume was to be considered. The floating fraction was homogenized and a 1-ml subsample extracted and filtered on quartz fiber GF/A Whatman filters (1.6 µm, 47 mm).

All fibers were observed according to the protocol presented in Chapter 2, and a subsample of n = 28 fibers randomly selected among indoor fibers was analyzed in ATR mode with the stereomicroscope in order to estimate the proportion of synthetic and natural fibers.

1.2 Description of the samples and the fibers

All of the filters for every type of sample contained fibers, most likely due to the fact that fibers can easily tear from clothing and some house furniture (polyamide, polyethylene-terephthalate or polypropylene carpets, curtains, textiles, etc.). Plastic fragments were not found on any sample; spheres were also absent.

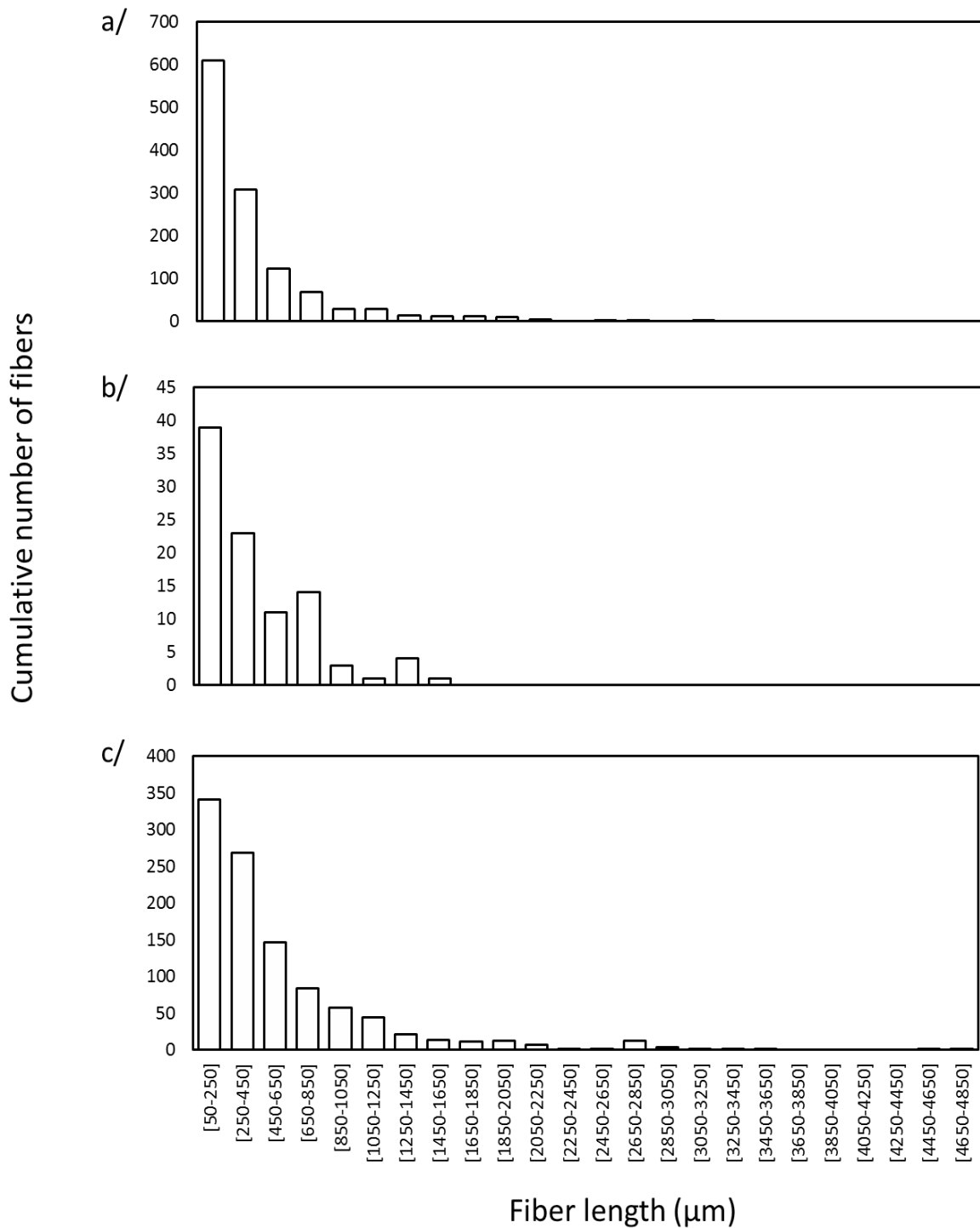


Figure 26: Total number of fibers observed in each size range between 50 and 4850 μm in various samples, a/indoor air, b/outdoor air, c/dust fall.

The figure 26 shows the size distribution of all fibers collected in indoor and outdoor air, as well as in dust fall. A similar pattern was observed in all compartments, with a majority of submillimeter fibers. A decrease in the number of fibers moving towards the larger sizes is noticed. The difference between compartments lies in the size of the longest observed fibers:

while fibers in the range of 4,650-4,850 μm can be found in dust fall, no fiber longer than 3,250 μm is observed in indoor air, and the size of fibers in outdoor air is always less than 1,650 μm . The fact that large-sized fibers are observed in dust fall is probably correlated with their size: larger fibers settle more rapidly and gather on soil surface, thus not staying suspended in indoor air. They are also less likely to re-suspend. Though fibers smaller than 50 μm were not counted due to the lower observation limit, the size distribution pattern suggests that much smaller fibers, likely to be inhalable, might be present in even greater concentrations.

1.3 Indoor and outdoor concentrations

Overall, indoor concentrations ranged between 0.4 and 59.4 fibers. m^{-3} , with a median value of 5.4 fibers. m^{-3} (Figure 27). Higher concentrations were recorded in Apartment A (2.5 - 18.2 fibers. m^{-3}) and the office (4.0 - 59.4 fibers. m^{-3}) compared with Apartment B (1.1 - 16.3 fibers. m^{-3}). The ANOVA test showed no influence of season on the concentration levels (p-value = 0.247, default statistical significance based on a $P < 0.05$ level for all tests), with these levels being site-dependent (p-value = 0.002). Mann-Whitney pairwise comparisons revealed no significant differences between Apartment A and the office (p-value = 0.053). Apartment B displayed statistically lower concentrations compared with Apartment A (p-value = 0.003) and the office (p-value < 0.001). Different building materials, furniture, cleaning habits and activities between the two apartments could explain this difference. Users were surveyed on their lifestyle in an attempt to explain this pattern. It did appear, for instance, that in Apartment A, clothes were being hung to dry in the living room, which might represent a major source. The office also experienced a high permanent occupancy level during sampling.

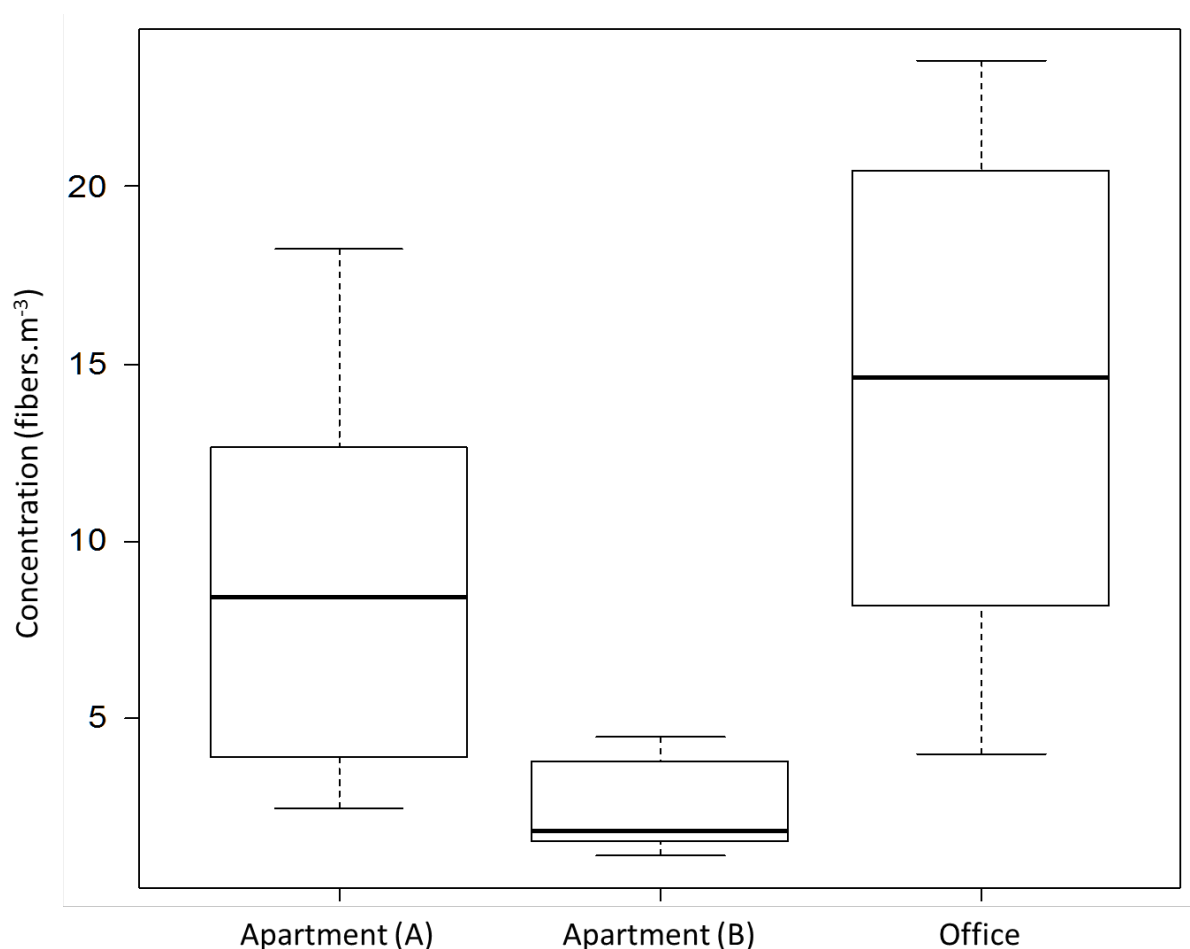


Figure 27: Concentrations of fibers in each of the three indoor sites (n=12). Boxplots are plotted from bottom to top with: [Lower quartile - 1.5*Interquartile range], [Lower quartile], [Median], [Upper quartile], [Upper quartile + 1.5*Interquartile range]. Outliers are displayed as isolated points.

Outdoor concentrations range between 0.3 and 1.5 fibers.m⁻³, with a median value of 0.9 fibers.m⁻³, and are significantly lower than indoor concentrations (Mann-Whitney, p-value < 0.001). Sampling took place during a winter rain event, and 5 times more fibers were collected on the filter, thus suggesting that rain produces a washout of fibers. If confirmed, it could be supposed that rainfall significantly alters the dynamics of fibers in the atmosphere, in producing a "scavenging effect".

1.4 Fibers in dust

As regards deposition rates, from 2.7 to 19.7 fibers.day⁻¹ were counted on filter surfaces (Figure 28), corresponding to a deposition rate of between 1,600 and 11,000 fibers.day⁻¹.m⁻². While the number of samples is too small to carry out any statistical testing, it can still be

observed that the deposition rate always remains lower in the office compared with both apartments for each season. Surprisingly, this finding is not correlated with the observed concentrations, which were lower in Apartment B.

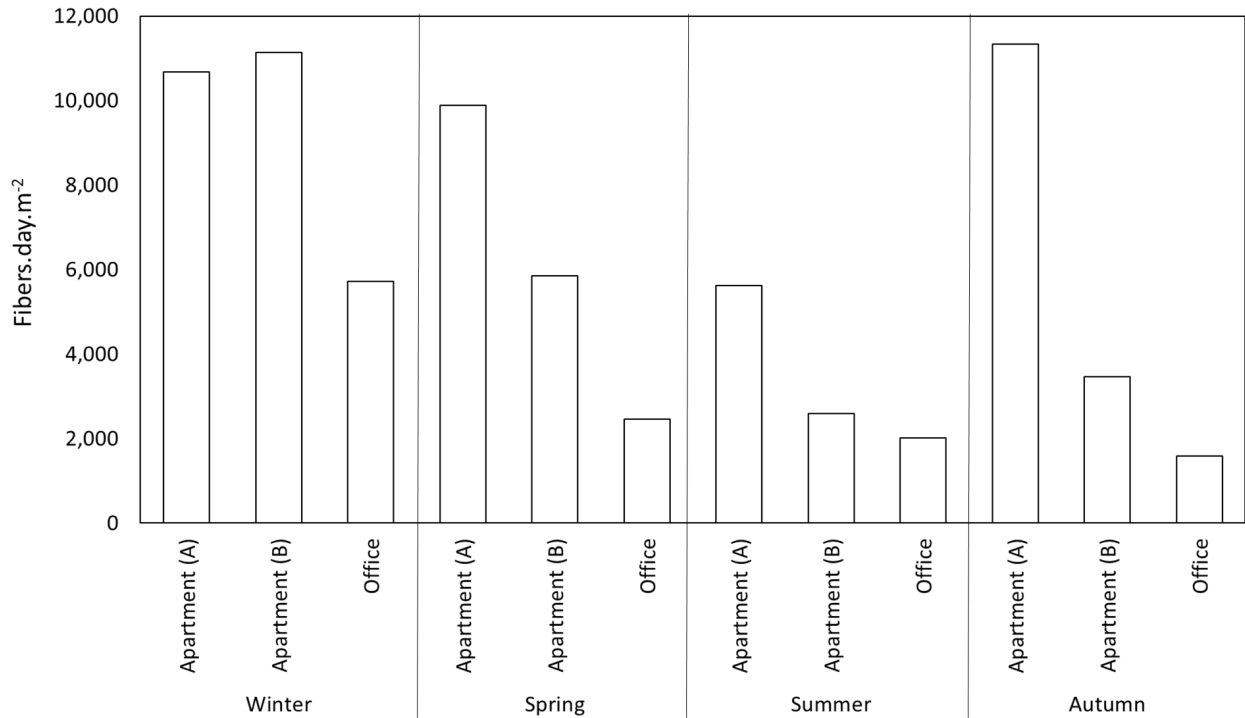


Figure 28: Deposition rate of fibers in the three sites at each season.

In addition to suggesting a potential accumulation of fibers on indoor horizontal surfaces in the form of dust, a significant probability exists, from a methodological point of view, that fibers present in the air fall onto samples during environmental laboratory analysis and contaminate them, which would underscore the importance of protecting samples from indoor contamination and conducting blank tests when studying microplastics. Considering the aperture diameter of the bottles used for treatment in our study (3.5 cm), it is estimated that the likely frequency of a fiber falling into a sample is once every 33 minutes (in assuming the higher measured deposition rate) provided the sample stays uncovered. When considering the lowest fiber deposition rate measured in the study, we conclude it takes more than 220 minutes for one airborne fiber in the sample to be contaminated. In taking into account the fact that these estimations were derived in an office and two apartments, which are supposedly more highly contaminated than a laboratory (due to the types of furnishings), plus the fact that samples spend very little time uncovered, this study has assumed that the

airborne contamination was negligible compared with the high number of fibers in the various compartments. This estimation must be carefully considered however given that any possible re-suspension of fibers from the filters has not been included herein.

Fiber concentrations in the dust collected in the apartments from vacuum cleaner bags vary between 190.0 and 670.0 fibers.mg⁻¹. A German study found an average dust deposition rate of 10.9 mg dust.day⁻¹.m⁻² (Seifert *et al.*, 2000). Based on this value and in considering that the fiber content of dust is similar in both studies, the fiber deposition rate is estimated at 2,070 to 7,300 fibers.day⁻¹.m⁻², which is fully consistent with our measured deposition rate.

1.5 Characterization of the fibers

As regards the composition of fibers in indoor environments, 67% are non-synthetic (natural and artificial), with the artificial cellulose-based fiber rayon being predominant. Acetate cellulose and wool were also encountered at times. The remaining 33% of fibers contain petrochemicals (plastic polymers) with one fiber being a mixture of polyamide (nylon) and cotton while the others are fully synthetic. The most recurrent polymer is polypropylene, which is consistent with the fact that houses and offices contain many potential sources of polypropylene (carpets, sofas, chairs, etc.). Polyamide fibers and copolymers of polypropylene and polyethylene were also detected. Surprisingly, polyethylene-terephthalate (polyester), which is one of the most widely used in the textile industry, was not detected in the subsample analyzed of indoor environment fibers.

2. Atmospheric fallout

This section is majorly based on an article we published in *The Marine Pollution Bulletin* in 2016:

Dris, R., Gasperi, J., Saad, M., Mirande, C., and Tassin, B. (2016). Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? Mar. Pollut. Bull.

2.1 Sampling approach

Total atmospheric fallout was collected at two sampling sites: one in a dense urban environment (University of Paris-Est-Créteil (48°47'17.8"N, 2°26'36.2"E) - Site 1 - Figure 29) and one in a less dense suburban environment (48°50'27.8"N, 2°35'15.3"E - Site 2 – Figure 29). The first site was the one used to estimate outdoor concentrations. Site 1 was monitored over a one-year period (from February 19th 2014 to March 12th 2015), while the monitoring at Site 2 lasted for a shorter period (October 3rd 2014 to March 12th 2015). Population density in the vicinity of Site 1 reaches 7,900 inhabitants.km⁻², i.e. twice that of Site 2, where it remains at 3,300 inhabitants.km⁻² ("Insee - *Régions, départements et villes de France*", 2011).

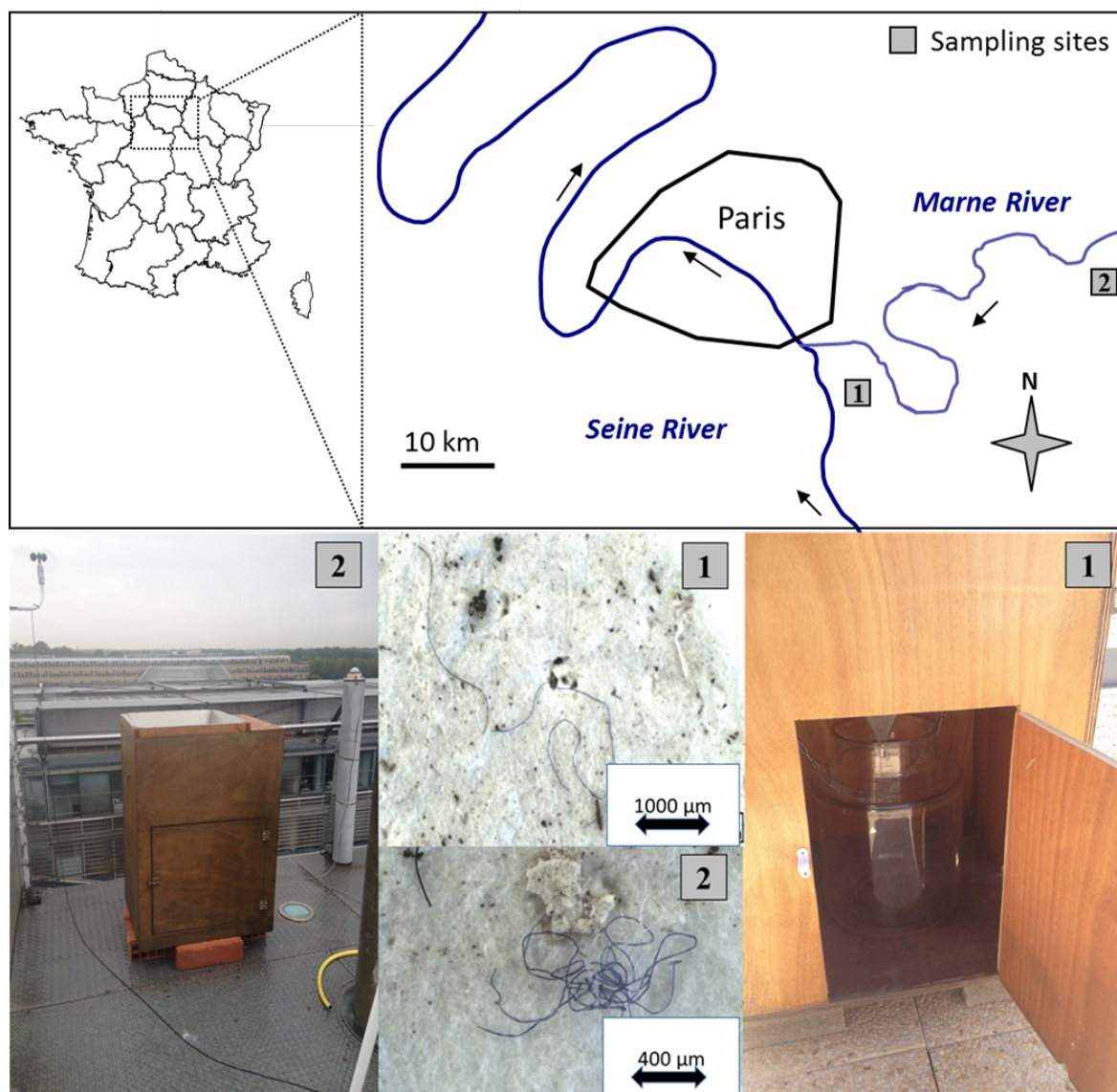


Figure 29: Localization, sampling device and synthetic fibers for each site.

The sampling surface was 0.325 m^2 , thus allowing for total atmospheric fallout (dry and wet deposition) to be collected through a stainless steel funnel. A 20-liter glass bottle was placed at the bottom of the funnel in an opaque box to collect the water. Samples were collected at various frequencies during the monitoring period, depending on cumulative rainfall, yielding 24 samples at Site 1 and 9 at Site 2. When both sites were being monitored, sample collection proceeded the same day for both sites in order to allow for comparison. No interruption of sampling occurred throughout the monitoring period at each site, hence providing a complete view of the annual variability of atmospheric fallout.

Each time atmospheric fallout was collected, the funnel was rinsed with 3*1 L of reverse osmosis water in order to recover all particles adhering to the funnel. As commonly practiced in studies focusing on pollutant fluxes in atmospheric fallout, preliminary tests demonstrated the efficiency of such rinses. Consecutive 1-L rinses showed that upon the fourth rinse, the number of fibers is similar to laboratory blanks (i.e. 0 to 2 fibers). After the rinsing step, collection bottles were immediately covered before being moved in order to avoid any contamination. Given the sampling period and collecting surface area, atmospheric fallout is expressed as a number of fibers per square meter per day. The amount of rainfall was recorded for both sites.

A subsample of $n = 30$ fibers was analyzed using Fourier Transform Infrared (FT-IR) micro spectroscopy (Lumos-Brucker microscope) coupled with an ATR (Attenuated Total Reflectance) accessory in order to characterize the proportion of synthetic and natural fibers and then identify the predominant plastic polymers.

2.2 Description of the samples and the fibers

Based on a long term monitoring (one year), our results show large amounts of fibers in the atmospheric fallout, which has not yet been reported in the literature. In a very limited quantity, some fragments or spheres were encountered during the monitoring. Their levels were too low to be considered and therefore neglected here.

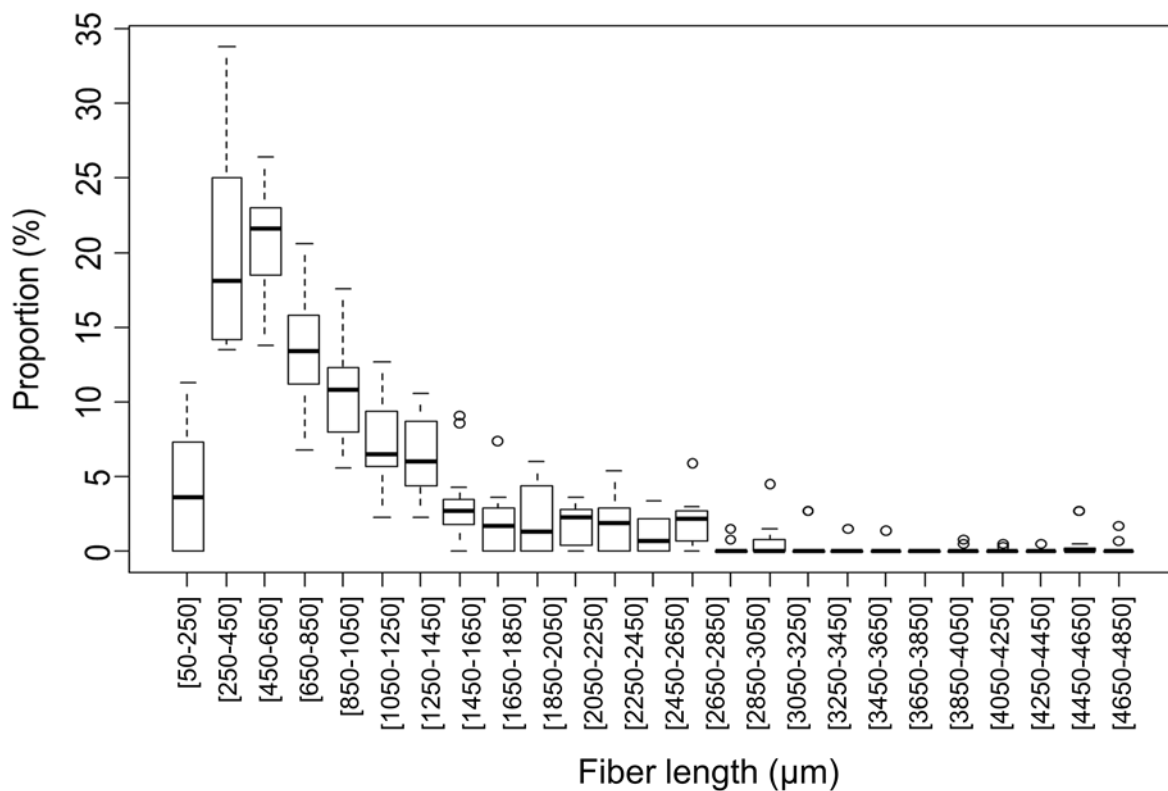


Figure 30: Size distribution of fibers in atmospheric fallout samples (site 1). Boxplots are plotted from bottom to top with: [Lower quartile - 1.5*Interquartile range], [Lower quartile], [Median], [Upper quartile], [Upper quartile + 1.5*Interquartile range]. Outliers are displayed as isolated points.

It can be seen from the size distribution (Figure 30) that the smallest fibers (in the 200 - 400 µm and 400 - 600 µm size ranges) are predominant, while fibers in the larger size ranges are rare. Few fibers were found in the 50 - 200 µm range. Fibers smaller than 50 µm were also observed with the stereomicroscope, but given that their nature is hard to identify, they were not taken into account. Fiber width was also measured during counting: fiber diameter varies between 5 and 100 µm.

2.3 Atmospheric fallout on the urban site

Throughout the year of monitoring (at Site 1), atmospheric fallout ranged from 2 to 355 fibers.m⁻².day⁻¹ (Figure 31), with an average of 110 ± 96 fibers.m⁻².day⁻¹ (mean ± SD), thus indicating a high annual variability. These values are significantly less than the fiber fallout previously assessed in indoor environments (Mann-Whitney, p-value < 0.001), a finding that is consistent with the lower outdoor air concentrations indicated previously.

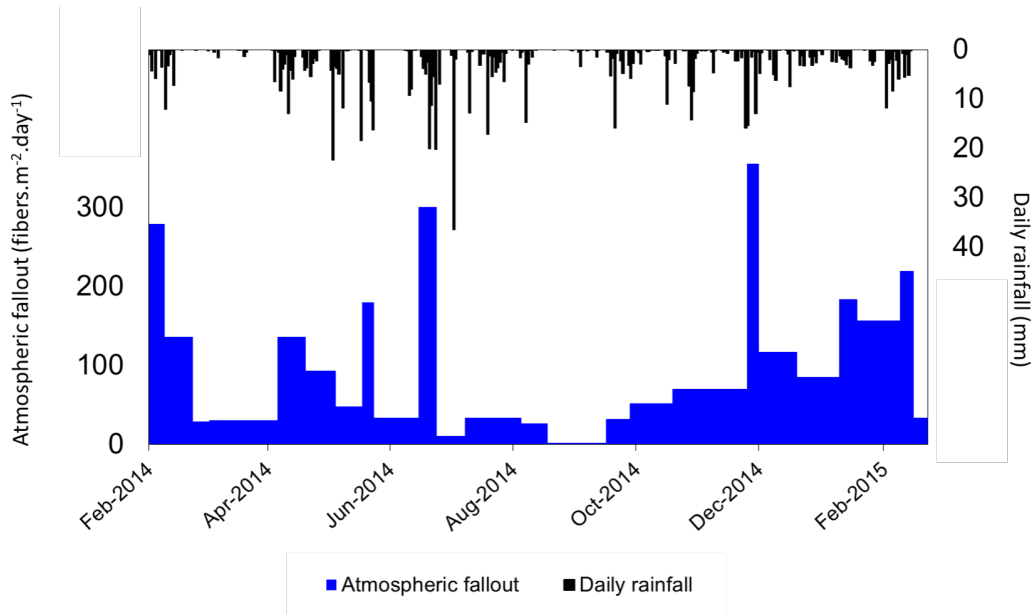


Figure 31: Atmospheric fallout of fibers on the site 1 in parallel with daily rainfall.

Rainfall seems to be an important factor influencing the fallout flux. In fact, an especially low number of fibers was found during dry weather or periods of limited cumulative rainfall. For rainfall of less than $0.2 \text{ mm}\cdot\text{day}^{-1}$, an atmospheric fallout between 2 and $34 \text{ fibers}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ was recorded. During rainy periods (i.e. 2 to $5 \text{ mm}\cdot\text{day}^{-1}$), highly variable levels of atmospheric fallout were encountered, ranging from 11 to $355 \text{ fibers}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. No statistically significant correlation was highlighted between the level of fibers in atmospheric fallout and mean daily rainfall, thus indicating that the absence of rain limits the fiber atmospheric fallout and moreover that rainfall height could be a significant factor, though clearly not the only one, contributing to fallout variability. Other mechanisms and time-varying factors also contribute to the fallout flux, yet they still need to be identified.

2.4 Comparison with a sub-urban site

At Site 2 (6-month monitoring program), the atmospheric fallout equaled roughly $53 \pm 38 \text{ fibers}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ (mean \pm SD).

When the levels at both sites are compared side-by-side, it can be observed that over all the monitoring periods, the suburban site systematically shows fewer fibers than the urban site (Figure 32). Statistical tests have revealed a significant difference between the atmospheric fallout on urban and suburban sites (Wilcoxon matched pairs test, confidence level of 5%, p -

value = 0.007). One potential reason for this difference pertains to the density of the surrounding population, which is considered as a proxy of local activity. This hypothesis needs to be confirmed at other sites in the Paris Metropolitan Area, as well as other sites in the world.

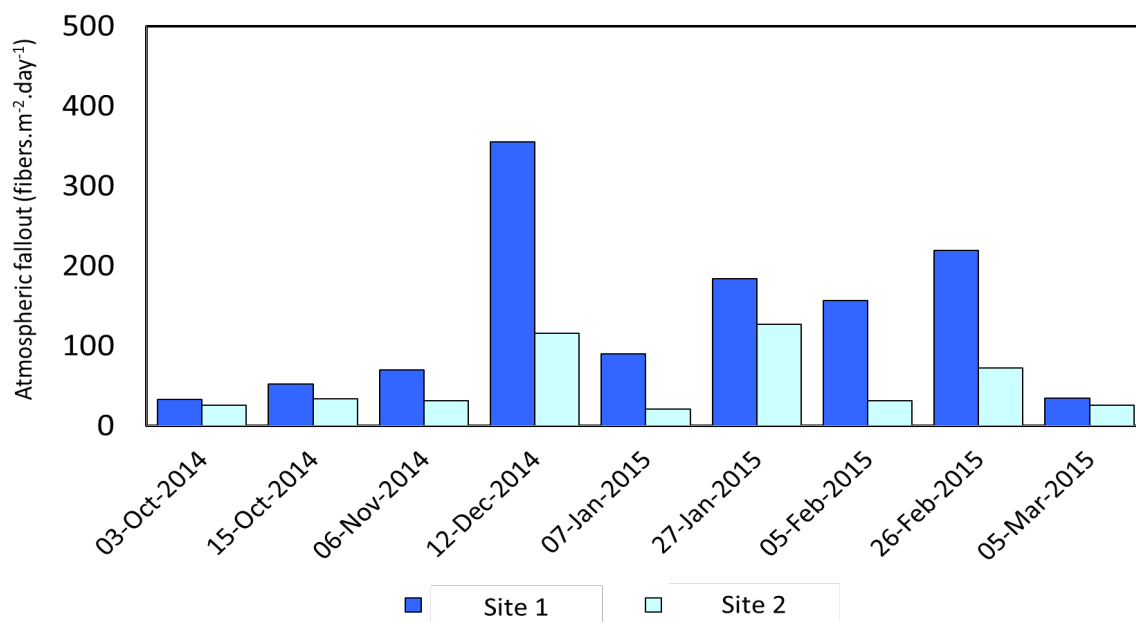


Figure 32: Atmospheric fallout of microplastics on an urban site (site 1) and a sub-urban site (site 2).

2.5 Characterization of the fibers

Fourier Transform Infrared (FT-IR) spectroscopy indicated that 40% of the analyzed fibers were natural, cotton or wool for the most part, with the remaining fibers being man-made. 31% of all fibers were manufactured by transforming natural polymers (rayon or acetate from cellulose). In contrast, 17% of the fibers corresponded to purely petrochemical-based synthetic fibers, mainly polyethylene-terephthalate with only one polyamide fiber and one polypropylene fiber. The other 11% of fibers were made with a mixture of various materials including pure synthetics (i.e. mixture of polyethylene-terephthalate and polyurethane), with the fibers being a mix of natural and synthetic materials (cotton and polyamide). Petrochemicals were therefore found in nearly 28% of the fibers analyzed in atmospheric fallout.

II. Urban sources

1. Urban runoff

1.1 Sampling approach

The case of a suburban catchment with separate sewerage system (i.e. wastewater and runoff water being collected separately) was considered herein. At the outlet of an urban catchment (Sucy-en-Brie), stormwater was collected with an automatic sampler during 5 events (from October 2014 to March 2016). For one of these events, a duplicate was also carried out.

The Sucy-en-Brie (Sucy) catchment area extends 261 ha, and its impervious surface coefficient (ISC) equals approx. 27%. Sucy is a residential area with mostly small single-family dwellings and limited commercial and professional activity (except for groceries and small services).

Table 11: Urban catchment characteristics and description.

| Sites | Location | Area (ha) | ISC ¹ (%) | Land use |
|-------------|-------------------|-----------|----------------------|-------------|
| Sucy | Paris, South-East | 261 | 27 | Residential |

1) ISC = impervious surface coefficients (%), 2) Number of events sampled per family of compounds

Sampled volumes depended on rainfall and runoff intensities. It varied from 100 to 1,000 ml. Samples followed the complete treatment steps presented in the chapter 2.

1.2 Results

The size distribution shows a similar pattern in runoff and atmospheric fallout (Figure 30), meaning that more fibers are found in the smaller size ranges and fewer fibers towards the longer ranges (to avoid redundancy, the size distribution will only be plotted if different for the subsequent urban matrices).

Runoff concentrations at the catchment outlet ranged between 24 and 60 fibers.L⁻¹, with an average of 35 fibers.L⁻¹. In considering the rainwater volume collected during the atmospheric fallout experiments (estimated from rainfall) over each monitoring period, a median concentration of 40 fibers.L⁻¹ can be estimated. This value is consistent with runoff results

demonstrating the potential link between atmospheric fallout and runoff. In the atmospheric fallout however, concentrations significantly varied (from 3 to 2,100 particles.L⁻¹), depending on the dry weather period duration and the characteristics of rain events occurring during the monitoring period. Atmospheric fallout alone cannot directly explain the stormwater pollution. This comparison is limited because atmospheric fallout and runoff inherently imply two different spatial scales (runoff comprises the entire urban basin with its various surfaces) and were collected at completely different temporal scales (at the event scale for runoff, as opposed to predetermined collection periods for atmospheric fallout).

Table 12: Fiber and fragment concentrations on runoff samples.

| Sample | Volume (ml) | Fibers.l ⁻¹ | Fragments.l ⁻¹ |
|---|-------------|------------------------|---------------------------|
| 15th October 2014, first event | 1,000 | 39 | No fragment found |
| 15th October 2014, second event | 250 | 28 | No fragment found |
| 15th October 2014, second event (duplicate) | 100 | 60 | No fragment found |
| 20th February 2015 | 500 | 14 | 10 |
| 18th September 2015 | 300 | 47 | 10 |
| 03rd February 2016 | 250 | 24 | 16 |

The runoff, as opposed to atmospheric fallout, contained plastic fragments during three of the five sampled events, with white, yellow and blue fragments being predominant. For the most part, foams and irregular fragments were found. Concentrations of up to 16 fragments.L⁻¹ were estimated. While the number of fragments was systematically lower than the number of fibers, no correlation could be derived between both types of microplastics. Even though the number of samples is too small to be statistically significant, this trend could indicate that in runoff, fibers and fragments originate from different sources and are not related.

2. Greywater

2.1 Sampling approach

Washing machine effluent was collected at four volunteers' homes. The washing loads were run in their own machines using their own clothes (Deshayes, 2015). Three consecutive washes were tested. In the first one, washing was carried out in an empty machine. Water was collected and considered as a blank, but this step also served to rinse the washing machine of fibers that could have been stuck from previous use. The second wash was performed without clothes but instead by adding the detergent, in order to produce a more global blank including the effect of the detergent. This second wash also helped rinse the machine more thoroughly. During the third and last wash, volunteers ran a regular load including clothes and other items like blankets. To have a more realistic vision, participants were asked not to change anything from their normal washing process; therefore, clothes made with natural, artificial and synthetic fibers were all included, without any pre-selection. This study sought to be representative of typical washes carried out by the population.

One sample of floor wash was also analyzed to identify the presence of fibers. One of the volunteers was also asked to wash his floor (in the living room) without altering his normal protocol, including sweeping the floor before washing. Upon completion, instead of disposing the water, he sampled it directly in the bucket using a 250-ml bottle. This single sampling was performed in order to determine the potential of other greywater as a source of microplastics.

2.2 Results

Results for washing machines are illustrated in (Figure 33). During the first washing (empty machine), concentrations between 120 and 452 fibers.L⁻¹ were found. These fibers remain most likely from previous washings. During the second wash, fibers concentrations vary between 210 and 810 fibers.L⁻¹. When clothes are washed, concentrations between 8,850 and 35,500 fibers.L⁻¹ were encountered, confirming the large contribution of the clothes (Figure 33).

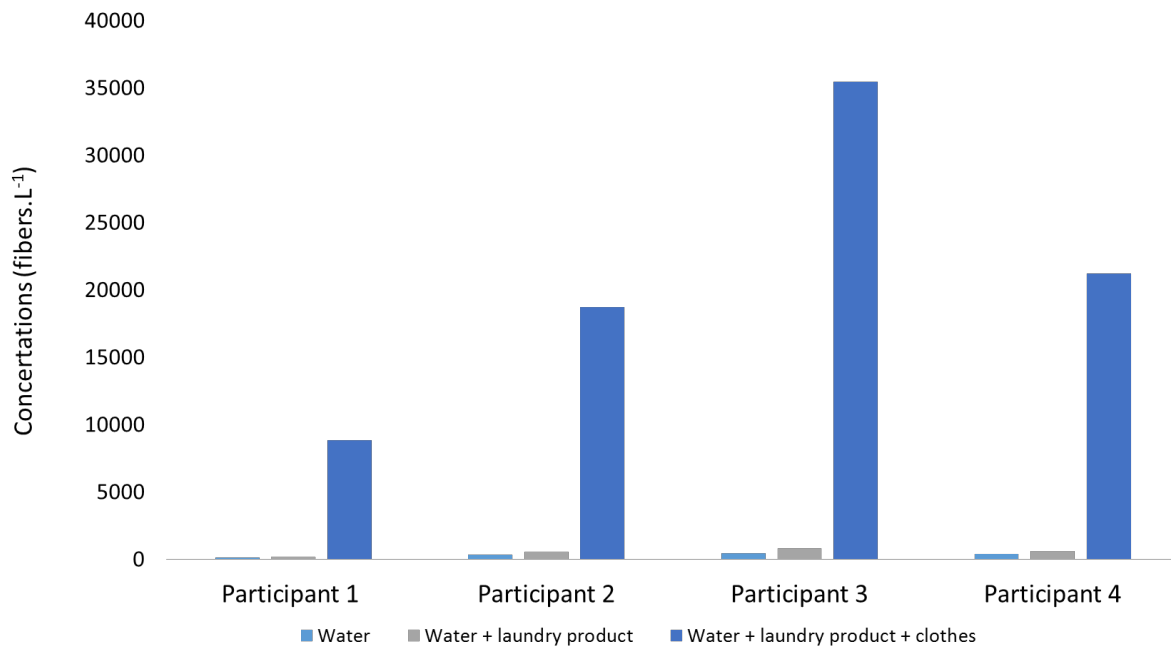


Figure 33: The number of fibers per liter in washing machines water for four volunteers, in three consecutive washes (empty washing machine, with product, and with product and clothes).

In accordance with observations from the indoor environment samples, no fragments were found in the floor cleaning sample and only fibers were detected, at a concentration amounting to 1,740 fibers.L⁻¹. While findings show that the fibers deposited on the floor from the indoor environment potentially enter the aquatic compartment, this contribution is considerably less than washing machine greywater. Not only are the concentrations lower, but it is also considered that just 0.5 L per inhabitant are used daily for floor cleaning, versus 14.4 L per inhabitant for washing machines (Deshayes, 2015).

3. Wastewater and wastewater treatment plant effluents

3.1 Sampling approach

Wastewater generated by the Paris Metropolitan Area is treated at several WWTPs. Four of these facilities, including the largest one, were considered in this work (Figure 34). In this figure, the WWTP capacity (in m³ per day) and type of wastewater treatment are provided. Since the facilities were not accessible, sampling was conducted by SIAAP (Parisian Public Sanitation Authority) staff. The effluent was conventionally collected, i.e. using an automatic sampler, and 24-hour averaged samples were considered. All samples were subjected to the protocol presented in Chapter 2.

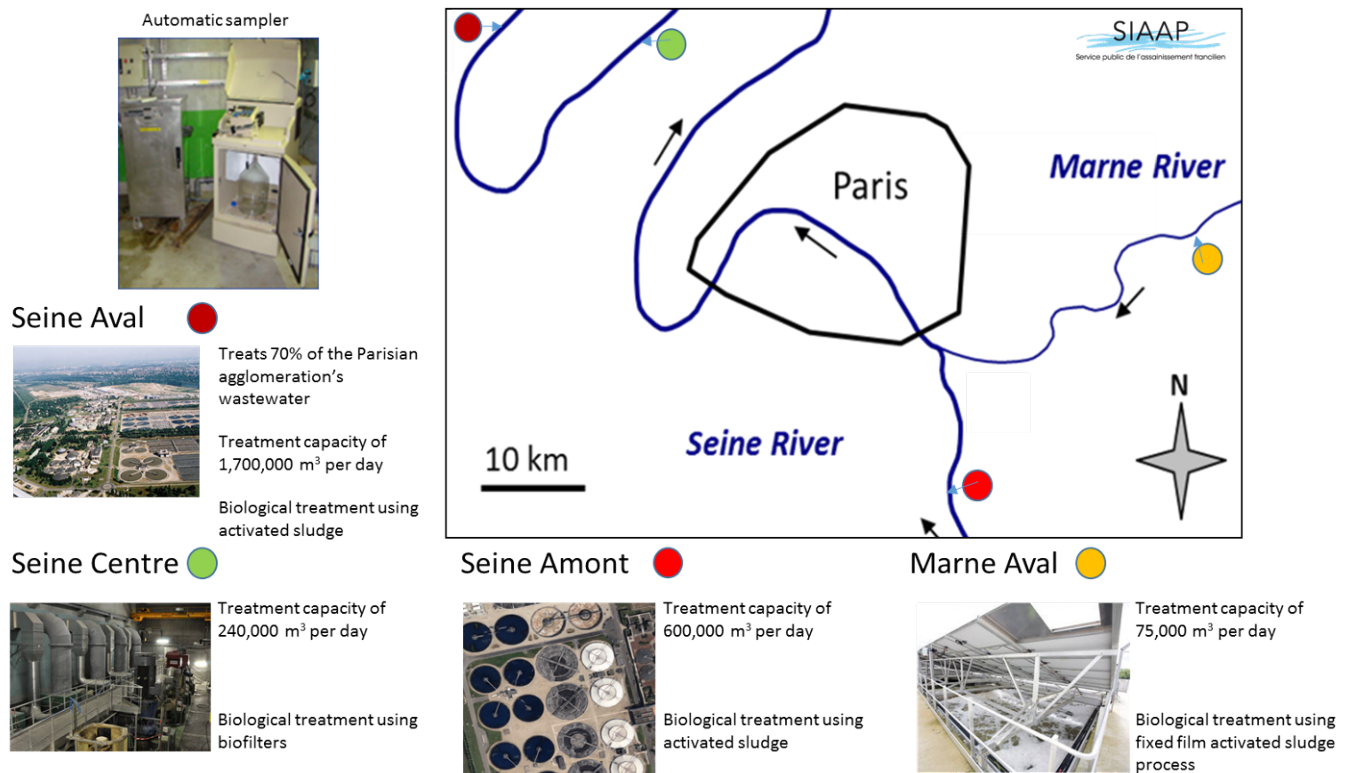


Figure 34: Location and description of the studied WWTPs accompanied with a picture of an example of the used automatic sampler.

For all four WWTPs studied, raw wastewater was collected during four different campaigns. The samples were not sieved, as opposed to previous studies investigating wastewater, hence the small fibers were not underestimated to the same extent (Carr *et al.*, 2012; Murphy *et al.*, 2016; Talvitie *et al.*, 2015). While automatic samplers were able to sample volumes of up to

20 L, this volume had to be shared with other scientific teams focusing on other pollutants. Only a limited volume of a homogenized subsample could therefore be studied (100 - 400 ml).

Two WWTPs were selected to estimate the treatment efficiency of two treatment processes. *Seine Centre* WWTP was considered for the case of treatment by biofilters, while *Seine Aval* WWTP is a conventional activated sludge plant. The *Seine Centre* treatment facility is located downstream of Paris and can treat up to 240,000 m³ of wastewater daily. The treatment process entails the following steps: water is pretreated (screening then grit and oil removal), then settled into a primary settling tank, before undergoing a biological treatment that involves the use of biofilters (Rocher et al., 2012). Three sampling campaigns were carried out on three consecutive days (8th, 9th and 10th April 2014). Raw wastewater after pre-treatment, settled wastewater and treated water were all considered for this analysis.

Seine Aval is the largest WWTP in Europe, with a daily treatment capacity of 1,700,000 m³. Wastewater undergoes a pre-treatment stage followed by primary settlement before entering the activated sludge process. The effluent is then clarified using a ballasted coagulation / flocculation process with lamella settling. An additional water treatment step consists of a Biostyr process, which combines total nitrogen removal with treated water clarification in a single stage. In this process, lightweight polystyrene disks are used as a floating medium for biofilm formation.

For this WWTP, two types of samples were extracted:

- For technical reasons, treated water was collected during just two of the four sampling campaigns mentioned above. A small, 250-ml subsample volume was considered for the first one and a larger, 2,500-ml volume for the second sample.
- In contrast, to provide a broader overview of the contamination, much higher volumes were incorporated using a different approach. Two samples were drawn from the treated water disposal channel. Since this channel is both wide and long enough to be navigable (Figure 35), a manta trawl with a 330- μ m mesh size was towed by a motorboat in the upstream direction for 10 minutes. Two samples were removed during two campaigns conducted on 17th September and 14th October 2015, with volumes of 67.7 m³. Only the fragments were counted in these samples.

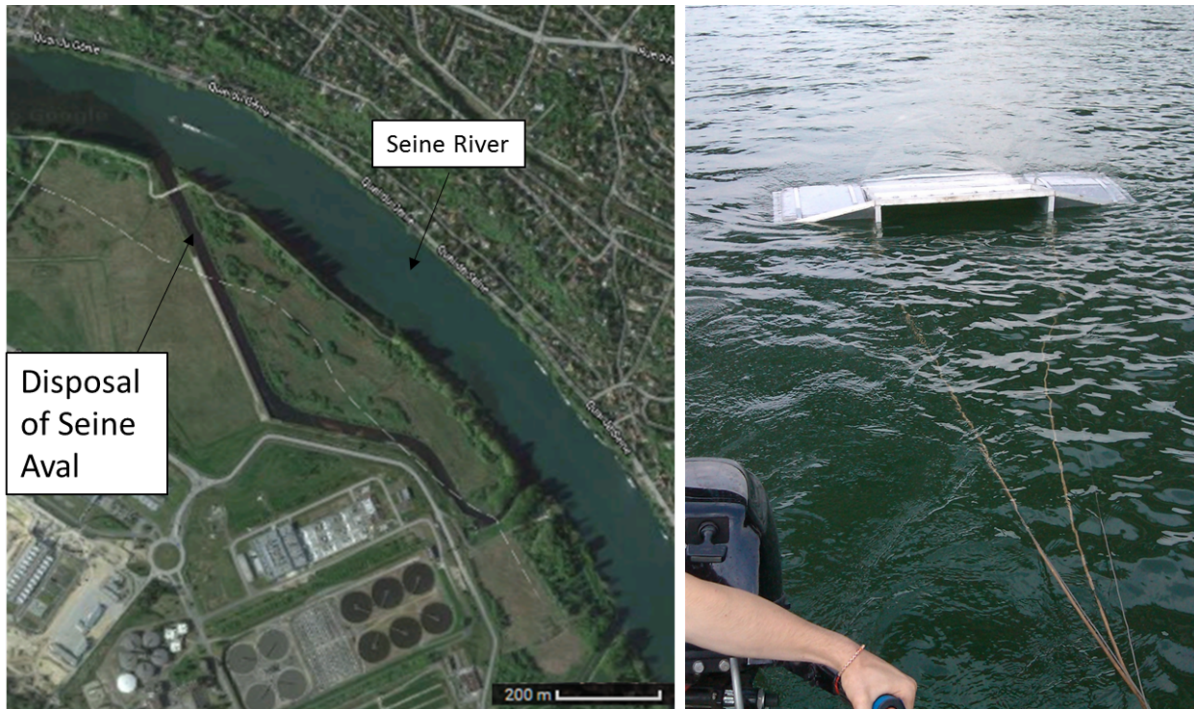


Figure 35: Disposal of Seine Aval and the used manta trawl.

3.2 Results

a. Raw wastewater contamination

A total of 20 wastewater samples were analyzed. In concordance to what was expected after the greywater analyses, wastewater are highly contaminated with fibers. The size distribution of the fibers is similar to the previous ones presented. Figure 36 shows the average concentration of fibers in wastewater at the entry of each of the WWTPs. The global average concentration is of 248 ± 109 fibers.L⁻¹ (mean \pm SD, n=20) reaching a maximum of 473 fibers.L⁻¹ in one sample of wastewater of Seine Aval. A previous study found 180 textile fibers (identified as plastics by FTIR) in one liter of wastewater (Talvitie et al., 2015) which is consistent with our results.

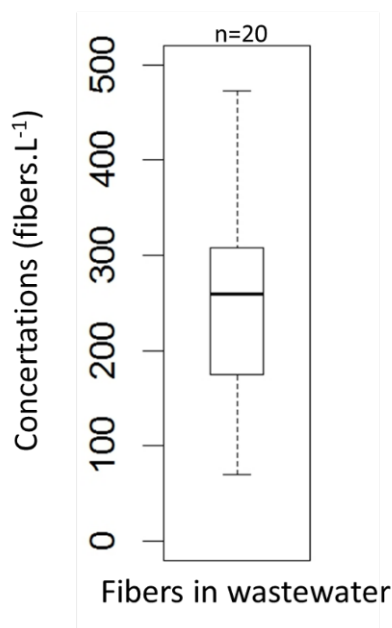


Figure 36: Concentrations of fibers observed in raw wastewater for four different WWTPs. The boxplot is based on n=20 samples with, n=5 on Marne Aval, n=5 on Seine Amont, n=3 on Seine Centre and n=7 on Seine Aval.

Unlike fibers, microplastic fragments were only rarely collected. In the 20 samples studied, 16 did not contain any fragments. For the four remaining samples, 3 contained just 1 fragment while the other contained two. The absence of fragments in the majority of samples does not imply however that wastewater is not being contaminated by this type of microplastic; it merely indicates a potential upper limit for the concentration of these particles. For instance, no fragments in a 400-ml sample implies a concentration < 2.5 particles.L⁻¹.

These results are in good agreement with another work presented at the MICRO 2016 conference showing that samples from a large London WWTP contained exclusively fibers (Maes *et al.*, 2016). In contrast, other works have observed fragments. A previous study indeed reported 430 particles.L⁻¹ (Talvitie *et al.*, 2015). A more recent study found 13 particles.L⁻¹, in excluding fibers (i.e. 15.7 particles.L⁻¹ reported with 18.5% fibers) (Murphy *et al.*, 2016). These studies all present very different concentration levels. Moreover, even with the small volumes analyzed in our samples, with levels similar to those listed in these publications, we should still have been able to observe more fragments.

Information is lacking for a determination of whether this pattern is site-dependent or related to the different methodologies employed. In a large sewerage network, fragments could settle

inside the sewer during dry weather periods and reach the WWTP only at low concentrations. This is possible given the fact that the Paris sewerage system is oversized, thus creating very low velocity and high particle sedimentation inside the sewer system, especially in zones upstream of the sewer. The absence of fragments could also be explained by the sampling process: the automatic sampler intake in fact always lies below the water surface while the fragments, often composed of polymers lighter than fibers, could be floating. The sampler inlet, also placed in wastewater, is always protected with a strainer in order to avoid pump obstruction. Though unknown, the precise mesh size of the strainer is still several millimeters, which theoretically exceeds the fragments and should hinder sampling. Yet many suspended solids are present in wastewater, which can clog the strainer in considerably reducing its mesh size and blocking the larger fragments. The pumping force is also unknown and needs to be considered herein as it may be too low to aspirate the fragments.

b. Wastewater treatment: case of Seine Centre

Similarly to the wastewater samples presented above, only limited volumes have been handled here. With the exception of one spherical particle in wastewater, only fibers were therefore observed in these samples. Fibers were found at high concentrations (from 260 to 320 fibers.L⁻¹) in pretreated wastewater, with 45% exceeding 1,000 µm. After primary treatment (physicochemical lamellar settling), concentrations between 50 and 120 fibers.L⁻¹ were observed along with a decrease in fiber size (Figure 37: the size distribution was plotted differently for these compartments in order to better highlight this pattern of decreasing size). Larger particles drastically decreased, thus attesting to their removal. In fact, only 7% were in the millimeter size range. At this stage of the treatment, fibers under 500 µm were predominant (66%). In the final effluent, the contamination level had decreased to 14 - 50 fibers.L⁻¹, and none of the observed fibers was longer than 1,000 µm.

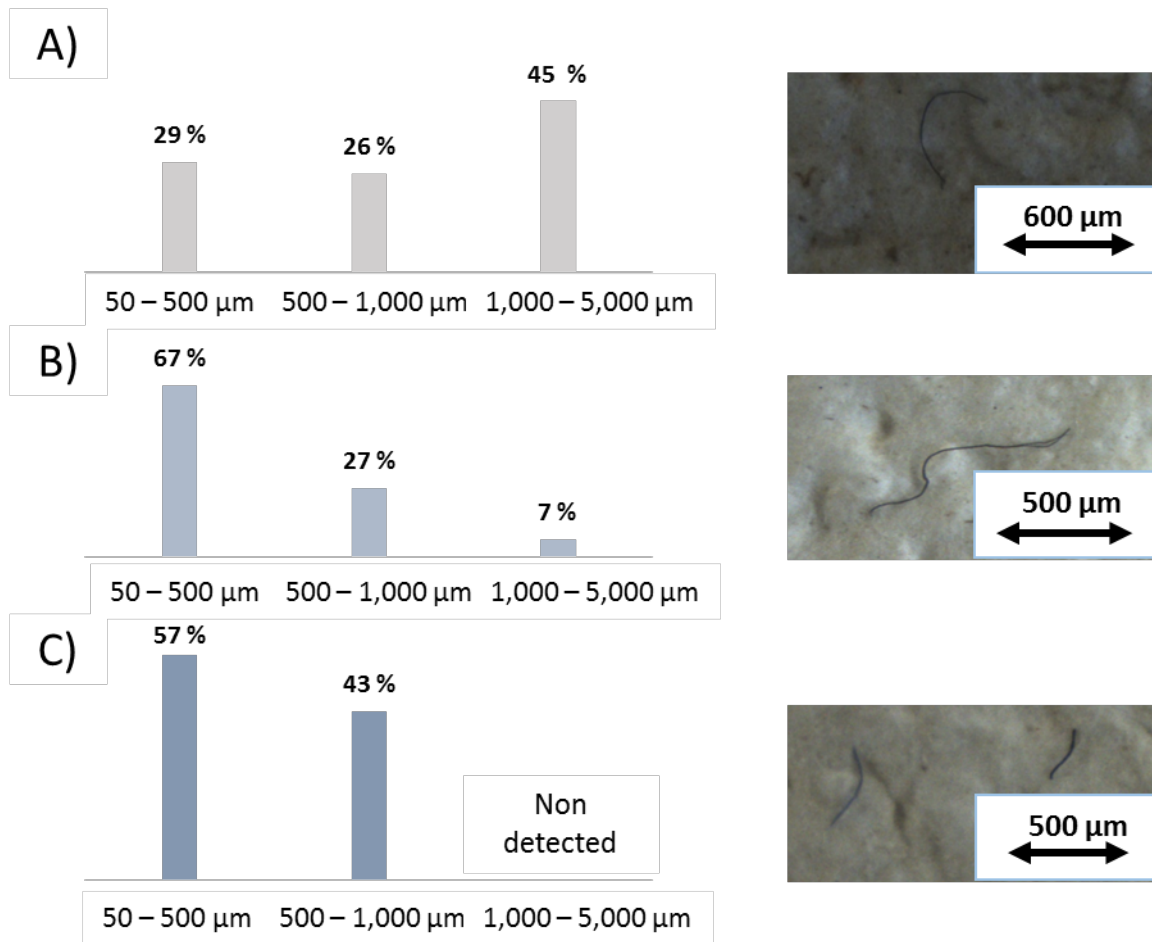


Figure 37: Size description and example of the fibers found in the WWTP of Seine Centre, with A) pretreated wastewater, B) after primary treatment step, C) treated water.

These results suggest a removal from 83 to 95% of the fiber contamination. As highlighted by the size pattern changes, water treatment in Seine Centre seems to be more effective at removing longer fibers that are absent from treated water.

c. Wastewater treatment: case of Seine Aval

Two 24-h averaged samples were considered, one of 250 ml the other of 2,500 ml. Both exhibited similar fiber concentrations with respectively 24 and 31 fibers.L⁻¹. The size distribution of fibers at the *Seine Aval* outfall differs from that observed for the *Seine Centre* outfall. With 41% of the fibers at the millimeter scale (i.e. larger than 1,000 μm), the size distribution is in fact similar to that found in wastewater. As opposed to *Seine Centre*, it could thus be supposed that the treatment methods used at *Seine Aval* are not size-selective. While treatment with biofilters is more efficient with respect to the larger fibers, activated sludge appears to reduce the pollution without affecting the size distribution.

Using the concentrations in wastewater estimated for samples collected during the same campaign (Figure 34), a removal efficiency of between 80% and 89% by the *Seine Aval* WWTP can be estimated. This efficiency as well as the final contamination levels in discharged effluent are of the same order of magnitude for both studied WWTPs. A proportion of the reduced fiber content has likely been transferred to the sludge (Habib *et al.*, 1998; Zubris and Richards, 2005); this compartment was not studied herein and requires further investigation.

Other works showed higher microplastic removal efficiencies by wastewater treatment plants, i.e. between 95% and 99% (Carr *et al.*, 2016; Murphy *et al.*, 2016). These results are only remotely comparable with ours since those studies included both fragment and microplastic fiber removal in the estimates and did not consider them separately. However, with the large-sized mesh sieves used (65 and 45 μm), the fibers could have been underestimated. On the other hand, more fragments were observed, thus indicating that the higher removal efficiency calculated is more closely correlated with the removal of fragments than with the removal of fibers. The removal protocol presented in our work applies strictly to fibers.

Since the sampling method used in the present study has not allowed for any significant observation of the fragments, which must be included when addressing the issue of microplastics, we proceeded with a manta trawl sampling inside the *Seine Aval* outlet channel in order to integrate larger volumes (68 m^3).

Irregular fragments were primarily observed, with foams, films and spheres being found on occasion. The number of fragments identified in this treated water amounted to 6×10^{-5} fragments. L^{-1} for one campaign and 3×10^{-4} fragments. L^{-1} for the other.

The fragment concentration levels were much lower than the fiber concentration levels observed in the samples extracted automatically (10^5 more fibers). Observing fragments on the manta trawl offers another indication of the fact that fragments are present in WWTP effluent yet at concentration levels too low to be detected in small volumes. Given that this sampling method cannot be used for wastewater, we did not proceed with an estimation of microplastic fragment removal by the WWTP.

4. Combined sewer overflows

4.1 Sampling approach

A combined sewer system collects rainwater runoff and domestic sewage in the same collector. During heavy rainfall events however, the volume of water exceeds the sewer capacity and can cause flood events. In this situation, untreated water is discharged directly into the receiving water bodies. Combined sewer overflows (CSOs) only occur during certain events, but the volumes considered are indeed high.

In this context, three samples were collected at the *La Briche* CSO outlet during different events; 500-ml volumes were considered and treated according to the regular protocol (Chapter 2).

Table 13: The three collected events with the analyzed volumes and the data related to the events.

| Event | Sample volume (ml) | Discharged volume (m ³) | Average flow (m ³ .s ⁻¹) | Conductivity ($\mu\text{s.cm}^{-1}$) | Rainwater (%) |
|---------------------------------------|-----------------------|--|--|---|------------------|
| 16th septembre 2015 | 1500 | 253,820 | 12.86 | 390 | 76 |
| 27th March 2016 | 500 | 73,812 | 3.15 | 350 | 80 |
| 11th May 2016 | 500 | 102,523 | 4.38 | 630 | 53 |

The conductivity was used to estimate the contribution of each, rainwater and wastewater in the final effluent. This approximation is based on the hypothesis that wastewater presents a conductivity between 1050 and 1170 $\mu\text{s.cm}^{-1}$ while the rainwater presents a conductivity between 80 and 150 $\mu\text{s.cm}^{-1}$ (Gasperi, 2006).

4.2 Results

Both fragments and fibers were encountered in the CSO samples. For fibers, levels of 190, 898 and 1,046 fibers.L⁻¹ were recorded (Table 14). The presence of fibers is most likely due to the combined contributions of both wastewater and runoff. The levels found in CSOs are higher than those in separated runoff. For two of the three samples, concentrations were higher than those in wastewater. Particle settlement during dry weather periods and particle re-suspension as flow increases were described in the literature (Gasperi *et al.*, 2009). A similar behavior could be expected for the fibers. The density is completely different for fibers and microplastics, and further work is needed to verify whether they actually undergo this process. Even if their density is less than some particles, the flocs that form in wastewater could trap particles and cause them to settle.

Fiber levels would also depend on the previous events. The cumulative rainwater amount over the five-day period preceding each sampling indicates 112 mm for the first event while just 13 mm and 16 mm were recorded for the other events. The sampling on 16th September 2016 was thus conducted after a long period of heavy rainfall, which might have induced a decrease in the quantity of fibers within the sewer system.

Table 14: Fibers and fragments concentration on the CSO samples.

| Event | Fibers.L ⁻¹ | Fragments.L ⁻¹ |
|---------------------------------------|------------------------|---------------------------|
| 16th Septembre 2015 | 190 | 35 |
| 27th March 2016 | 1046 | 3100 |
| 11th May 2016 | 898 | 658 |

Levels of fragments vary between 35 fragments.L⁻¹ and 3100 fragments.L⁻¹. The reached levels are especially high even if it's not systematic. Lower concentrations of fragments in comparison to fibers can be observed except for the event of 27th March which is also the one presenting the highest rainwater contribution and volume.

III. Fiber fluxes in different compartments

Given the lack of studies and data addressing the issue of fiber and plastic sources and fluxes in urban areas, it is difficult to evaluate the significance of the various sources.

This section seeks to estimate the number of fiber fluxes at the scale of the Paris Metropolitan Area, as defined in Chapter 2 (a land area of approx. 2,500 km² - 10 million inhabitants). By adopting several hypotheses, the proportion of synthetic fibers (microplastics) could be evaluated. The number of microplastic fibers was then used to estimate the mass fluxes. Since the fibers were actually measured, the cumulative total fiber length was calculated. Next, this length was coupled with the approximated fiber diameter in order to derive the total fiber volume. It was assumed that diameters ranged between 5 and 100 μm, with an average of 25 μm. With the total volume and specific densities of the plastic polymers (1 g.cm⁻³ for PA and 1.45 g.cm⁻³ for PET, i.e. corresponding to two low-density heavy plastic polymers widely used in the textile industry), total masses could thus be estimated. Results are presented in tabular form at the end of this section (Table 15).

According to the average atmospheric flux of total fibers on both the urban and suburban sites (respectively 110 and 53 fibers.m⁻².day⁻¹), it can be extrapolated that at the scale of the Paris Metropolitan Area, between 1.2 x 10¹¹ and 2.5 x 10¹¹ fibers, including microplastics, could originate annually from the atmosphere. According to the FTIR analyses conducted, it can be extrapolated that 30% of the fibers do in fact contain plastic polymers. Between 3.5 x 10¹⁰ and 7.6 x 10¹⁰ microplastics would thus fall per year from the atmosphere onto the Paris Metropolitan Area. The masses of plastic fibers originating annually from the atmosphere at the metropolitan scale are likely to lie between 6 and 17 metric tons.

For greywater, it can be estimated that France generates 14.4 L of water per inhabitant that flow daily from washing machines into the wastewater system (this figure was provided by *Eau de Paris*, which is the public operator in charge of drinking water production and distribution in Paris). At the Paris Metropolitan scale, in considering the minimum and maximum concentrations recorded, it is assessed that between 4 x 10¹⁴ and 2 x 10¹⁵ fibers are discharged annually into the wastewater stream. However, this work did not provide a chemical characterization of washing machine fibers. It can be assumed that at a global scale,

60% of these fibers are synthetic, in judging by European uses (Chapter 1). The only factor that might alter this figure is the fact that natural fibers could tear off more easily from clothing than synthetic fibers and therefore become predominant. According to Liorca *et al.* (2016), microplastics account for 5% of total washing machine effluent. Based on both hypotheses (5% and 60% synthetic fibers), between 2×10^{13} and 10^{15} microplastic fibers are therefore being discharged annually into the Paris Metropolitan wastewater, which corresponds to a mass ranging from 6 to 437 metric tons per year.

Knowing that the SIAAP treats 2.3 million L of wastewater daily for the Parisian Metropolitan Area, it can be evaluated that between 6×10^{13} and 4×10^{14} fibers flow annually into the wastewater system. By adopting the hypothesis that the proportion of synthetic fibers remains constant between washing machine disposal and wastewater treatment plant entry, between 3×10^{12} and 3×10^{14} of this estimation correspond to synthetic fibers, which would mean that a mass of 2 to 225 metric tons of fibrous microplastics flow annually in wastewater.

By applying the estimated removal rates on both WWTPs (i.e. between 80% and 95%) to the global estimation provided above for wastewater, it is estimated that the Paris Metropolitan Area releases between 2×10^{11} and 5×10^{13} microplastic fibers into surface waters annually, thus corresponding to a mass of between 0.1 and 45 metric tons.

It was also estimated that CSOs in the Paris combined sewerage system reach nearly 21 million m^3 annually (Cladière *et al.*, 2011). This finding indicates the potential introduction into freshwater of between 4×10^{12} and 5×10^{12} fibers annually. An accurate estimation of the proportion of plastic polymers from among these fibers would be difficult to provide, which may be a reflection of the proportions estimated either for atmospheric fallout (30% synthetic fibers) or at the WWTP (between 5% and 60% synthetic fibers). Due to the high level of uncertainty such hypotheses could imply, it was decided not to attempt an estimation of the total microplastic fibers input by CSOs.

Table 15: fluxes of fibers and synthetic fibers in the different urban compartments.

| Compartment | Total flux of fibers (fibers per year) | Hypothesis of synthetic fibers (%) | Flux of synthetic fibers (fibers per year) | Flux of synthetic fibers (Metric tons) |
|--------------------------|---|---------------------------------------|---|---|
| Atmospheric fallout | $1.2 \times 10^{11} - 2.5 \times 10^{11}$ | 30 | $3.5 \times 10^{10} - 7.6 \times 10^{10}$ | 6 – 17 |
| Washing machine disposal | $4 \times 10^{14} - 2 \times 10^{15}$ | 5 – 60 | $2 \times 10^{13} - 10^{15}$ | 6 – 437 |
| Wastewater | $6 \times 10^{13} - 4 \times 10^{14}$ | 5 – 60 | $3 \times 10^{12} - 3 \times 10^{14}$ | 2 – 225 |
| WWTP disposal | - | - | $2 \times 10^{11} - 5 \times 10^{13}$ | 0.1 – 45 |

IV. Discussion and conclusions

This chapter has investigated various urban compartments, highlighting the ubiquity of fibers in all compartments studied, while fragments seem to be encountered mainly in urban runoff and CSOs.

First of all, fibers including microplastics were detected in indoor compartments, whether they be in indoor air, dust fall or settled dust. To a much lesser extent, they were also present in outdoor air.

Results show that human exposure to natural and synthetic fibers may occur in indoor environments. A study has observed human lungs with a microscope (Pauly *et al.*, 1998), in finding that 87% of the studied lungs (n=114) contained fibers. Cellulosic and plastic fibers were both observed. Moreover, this same study revealed that 97% of malignant lung specimens contained fibers. The fiber length was primarily in the neighborhood of 50 μm yet could reach a length exceeding 250 μm . The risk of inhaling microplastic particles and fibers was recently addressed (House of Commons' Environmental Audit Committee Oral evidence: Environmental impact of Microplastics, HC 925, Monday, 9 May 2016). Moreover, these fibers may contribute to human exposure through ingestion of settled dust, particularly by young children due to their frequent hand-to-mouth contact. Smaller inhalable fibers (down to the nanofiber scale) may also be present in indoor and outdoor air, but these fibers could not be counted with the method used herein. No data or information is currently available to prove the potential human health effects of ingested or inhaled microplastics. Further research is thus needed, particularly regarding the impact of both plastic and natural fibers as well as the effects of the pollutants and additives these fibers carry.

Much higher concentrations of fibers were found in indoor air compared with those measured outdoors. It is possible that a fraction of the fibers are transferred from indoors to outdoors through the air exchange rate, which could contribute to atmospheric fallout, hence demonstrating that indoor air also acts as a microplastic source. Moreover, fibers settled onto indoor surfaces are most likely released in wastewater, e.g. when cleaning floors. Both indoor and outdoor air must therefore be taken into account to understand microplastic dynamics in an urban environment.

The atmospheric compartment was confirmed as a source of fibers, including microplastics, by means of analyzing atmospheric fallout. These microplastics may have different sources: synthetic fibers from clothes and houses, degradation of macroplastics, landfills or waste incineration. The characterization has indicated that the hypothesis of clothing being the main source of these fibers is the most plausible. These fibers in the atmosphere, including microplastics, could be transported by wind to the aquatic environment or deposited onto city land surfaces or agrosystems. After deposition, they could impact terrestrial organisms or be transported into the aquatic systems through runoff. More work is needed in order to investigate these atmospheric fibers and understand their origins, their ultimate destinations and the mechanisms and factors leading to their transport and fallout. The distance over which a fiber may be transported is still unknown. In this study, it cannot be concluded whether the observed fibers originate from sources in close proximity or more distant places. Microplastics were found in isolation, thus suggesting that transport might be occurring over long distances (Free *et al.*, 2014). This work has not been intended to provide accurate atmospheric fluxes for microplastics since many uncertainties remain and more studies are required; it has however served to highlight the important role this source may play in continental and marine environments and moreover encourages scientists to pay greater attention in subsequent research.

As a follow-up, fibers were quantified and confirmed to be present in urban runoff water. In addition to atmospheric fallout, other sources must be taken into consideration. For instance, activity of the local population is likely to be a closer source. Fibers can be deposited directly from clothing worn by people walking in the street without being transported by wind or being part of atmospheric fallout. In contrast, the fibers originating from dry weather atmospheric fallout could be re-suspended by wind or washed away during road and street cleaning, thus limiting the accumulation between two rain events. This work has not provided a deep-rooted understanding of runoff-related mechanisms yet still serves as an indicator of this potentially major source.

While only fibers were detected in atmospheric fallout, the runoff also contained fragments. This difference might be due to the size and volume of the fragment particles. In the geosciences, models are available to predict whether a particle can undergo suspension,

saltation (aerial transport but over small distances at very low heights) or no wind transport (Valance *et al.*, 2015). These models, although developed for higher-density particles (e.g. sand at 2.65 g.cm^{-3}), can still inform that the main characteristics involved in predicting the potential of a particle to be suspended in air are its size, shape and the wind velocity. Our work has shown, within the size range analyzed and under Paris wind conditions, that fibers can be transported by air while the larger fragments seem to fall directly onto surfaces and await transport by urban runoff, if not cleaned by road sanitation services.

WWTP effluent was also studied as a potential source of microplastics. Fibers were found in the disposal of washing machine effluent and, consequently, in wastewater. The mechanisms and dynamics that fibers undergo in a sewerage system are totally unknown. The roughly estimated flux of fibers entering WWTPs lies in the same range as the amounts supposedly discharged by washing machines. This estimation range however is broad, and fluxes might potentially be lower. Due to the overly limited time scale (max 48-72 h), any fragmentation process can be considered as negligible. On the other hand, a sedimentation process during dry weather periods within the sewerage network is entirely possible.

WWTP effluent was recently investigated by several authors, yet none have provided an idea of the contribution of WWTP disposal compared to other sources. It is apparent herein that the estimated number of microplastic fibers stemming from WWTPs, even with a fiber removal rate of between 80% and 95%, is higher than the fibers stemming from atmospheric fallout. Moreover, while WWTPs are discharged directly into freshwater, the high amount of fibers in atmospheric fallout will only partially reach the aquatic system. The very low fragment concentration observed indicates that WWTP discharges are major sources of fibers compared with other microplastics.

In contrast, CSOs contain high fragment as well as fiber concentrations. It appears that within urban environments, CSOs constitute the primary input of microplastic fragments into freshwater. Moreover, the fact of CSO displaying fiber concentrations that sometimes exceed those in wastewater tends to confirm a re-suspension of particles settling on the sewer.

Our knowledge of the various dynamics and mechanisms at play remains very limited. For instance, the conditions driving fiber suspension, aerial transport and fallout processes are all

unknown. With this work, we have been able to identify the fate of a non-estimated proportion of these fibers that will settle on urban surfaces. Afterwards, these fibers will be subject to urban runoff. Similarly, further knowledge is required on the fiber and fragment transport processes acting inside the sewer. Moreover, while the removal rates by two different WWTPs have been estimated, the removal mechanism is still poorly understood.

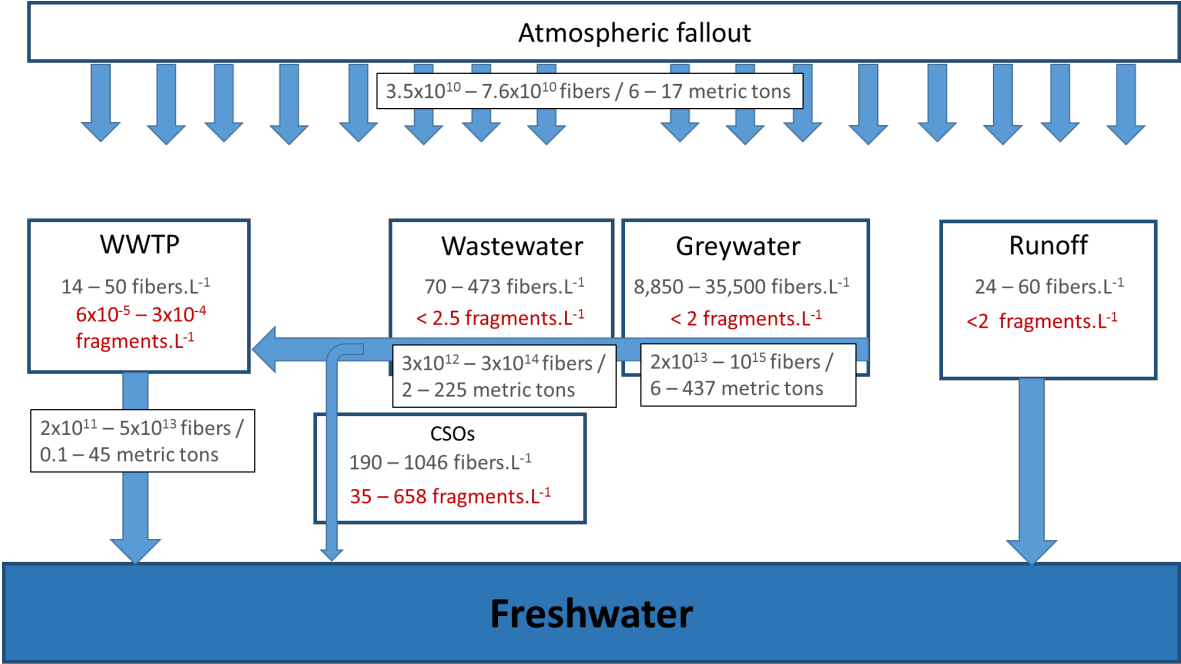
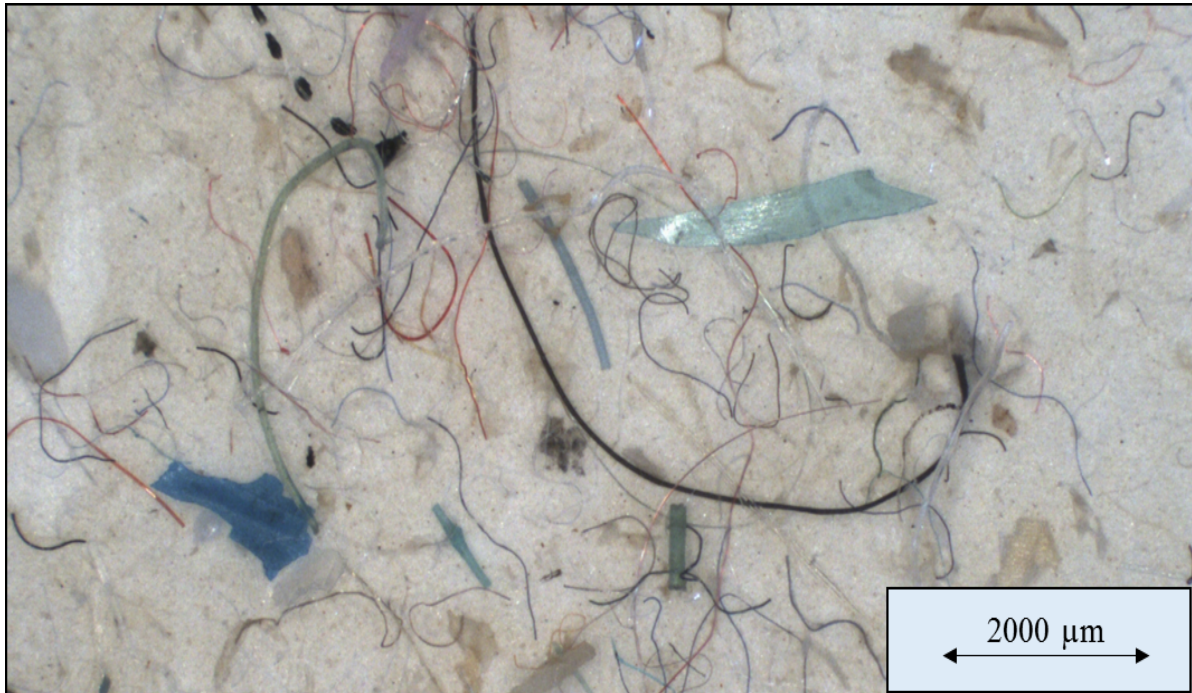


Figure 38: A synthesis of the total fiber and fragments concentrations in the investigated urban compartments as well as the fluxes of synthetic fibers between different compartments.

Chapter 5: Microplastics in urban rivers



Particles collected at Saigon in Ho Chi Minh City

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This chapter will assess river contamination by fibers and microplastic fragments. While various previous works have used different mesh sizes for their sampling nets, any survey of fibers and microplastics must, in our opinion, entail a continuous scaling size. In a preliminary study published during the early stages of this work, we tested two net mesh sizes (Dris *et al.*, 2015) and highlighted the differences between using a small size (80 μm) and a larger size (330 μm). Fibers are highly concentrated, making it preferable to use the 80- μm net since fibers easily pass through a larger-sized mesh, while fragments are less concentrated, thus requiring the sampling of greater volumes. In this chapter, both methods have been employed, namely:

- Short-term temporal variations of fiber concentrations are investigated with the 80- μm net. Spatial variability through the water section has also been verified. Both vertical and horizontal concentration profiles have been investigated herein.
- Monthly monitoring extending more than one year ($n=19$ campaigns) and at 5 stations both upstream and downstream of Paris was conducted with the 80- μm mesh size to gain an overall idea of fiber contamination in the Paris Metropolitan Area.
- Two different approaches were chosen to collect fragments with the 330- μm nets. Campaigns were carried out with a manta trawl towed by a boat downstream of Paris in order to provide results comparable with some literature findings. On the other hand, a campaign was conducted with a stationary net at the 5 annually monitored stations for comparison with the 80- μm approach.

I. Fibers: characterization, concentrations, fluxes

1. Sampling approach

1.1 Sampling device

Sampling was performed with a homemade device coupling a plankton net (mesh size: 80 μm - 725-cm² sampling surface area) with a propeller-type current meter (OTT - C2'10.150' - enabling measurement of water velocity in the range of 0.025 to 5 m.s⁻¹) (Figure 39). Although plankton nets are typically deployed vertically in freshwater to sample phytoplankton biomasses over a given depth, this net was modified to allow horizontally-flowing water through it. The local horizontal flow velocity was measured simultaneously in order to evaluate the sampled volume. A triplicate for velocity measurements is generally carried out.

Clogging during sampling may occur due to suspended matter in the Seine River. Preliminary tests revealed that the net was fouled when sampling surpassed 8 m³. Testing was held with suspended matter levels of between 10 and 42 mg.L⁻¹. Quicker clogging would be expected with higher suspended matter levels; to ensure the absence of clogging, the sampled volume was always kept well below the 8-m³ threshold, and the net was exposed for 1 minute as a compromise between increased representativeness, avoidance of clogging and the possibility of sampling between the relatively frequent barge traffic. The surface layer of the water column was taken into consideration (i.e. a 0.1-0.35 m layer).

Following collection, the net was thoroughly rinsed three times from the outside using river water. Before monitoring, during one sampling, rinsing efficiency was tested. The first three rinses revealed a cumulative number of 61 fibers, while just 2 fibers were found in the fourth rinse. This test also showed the small amount of fibers in a field blank.

All samples were subjected to the various analytical steps presented in Chapter 2 after sampling.

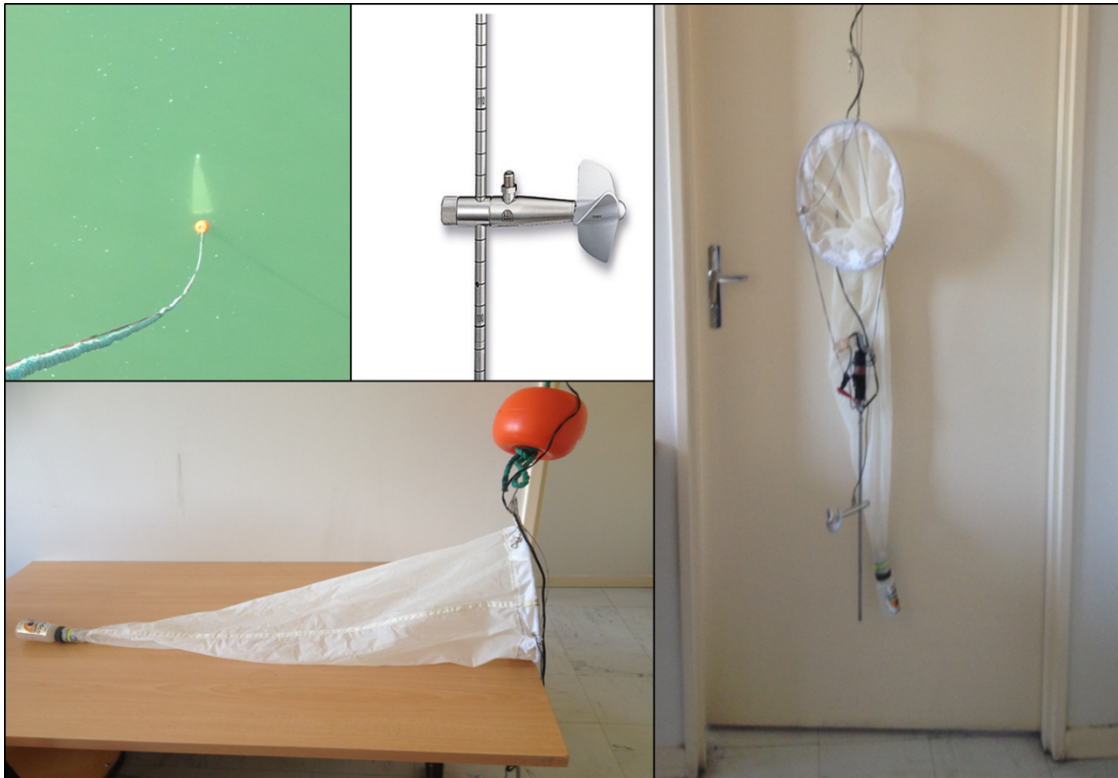


Figure 39: The 80 µm mesh size plankton net used in this survey with the propeller-type current meter.

1.2 Short-term temporal variability

Two separate campaigns were carried out in order to assess the short-term temporal variability of microplastic concentrations. During the first campaign held on 12th March 2015 at the P1 site (Figure 41), 6 samples were extracted over a 2-h period (10:52 am to 00:48 pm). Each sampling was performed for 1 minute. The average volume sampled equaled 2.21 m³. A river flow of 144 m³.s⁻¹ was recorded.

The second campaign was held on 6th July 2015 at the same site. A 3-minute duration was chosen for the 6 samplings. Regarding the low river flow of 24 m³.s⁻¹, we were able to increase sampling duration without causing any clogging. An average volume of 2.72 m³ was sampled. The first sampling occurred at 00:03 pm, while the last sample was extracted at 03:00 pm.

1.3 Spatial variability through the section

At P1 station, triplicates in five different points in the river section were sampled the 23rd April 2015 (flow of 69 m³.s⁻¹, duration of 3 minutes). Samples have been conducted just below the

surface (right bank, middle, left bank) and at different depths (1m and 2m depth) in the middle of the river (Figure 40). With an echo sounder, it was determined that the maximum depth of the water at the moment of the sampling was 2.6 m. All samplings were carried out within 3 hours.

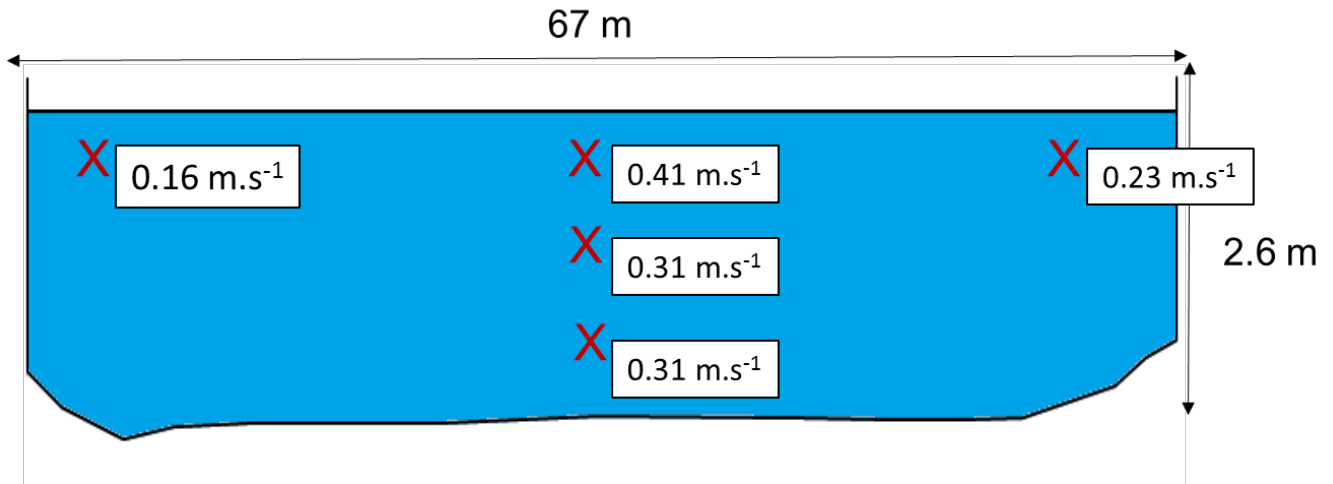


Figure 40: Sampling points of the section of the river with the corresponding measured water velocities.

1.4 Monitoring in the Seine and Marne Rivers

Once a month, beginning in April 2014, five samples were extracted at four stations (P2-P5) on the Seine River from upstream of Paris to downstream. One station on the Marne River (P1) was also considered (Figure 41). This monitoring was pursued until December 2015, except for January and August 2015, two months during which no sampling took place. This set-up led to 19 sampling campaigns (Figure 42). Sampling at the five stations was always performed on the same day. To ensure repeatability from one campaign to the next, the sampling duration was set at 1 minute, which ensured that the net would not clog regardless of the river flow and suspended matter concentration. The collected volumes ranged between 0.2 and 4.0 m³ over the one-year monitoring period. This monitoring would also yield an overview of concentrations under various water flow conditions varying from 21 to 856 m³.s⁻¹.

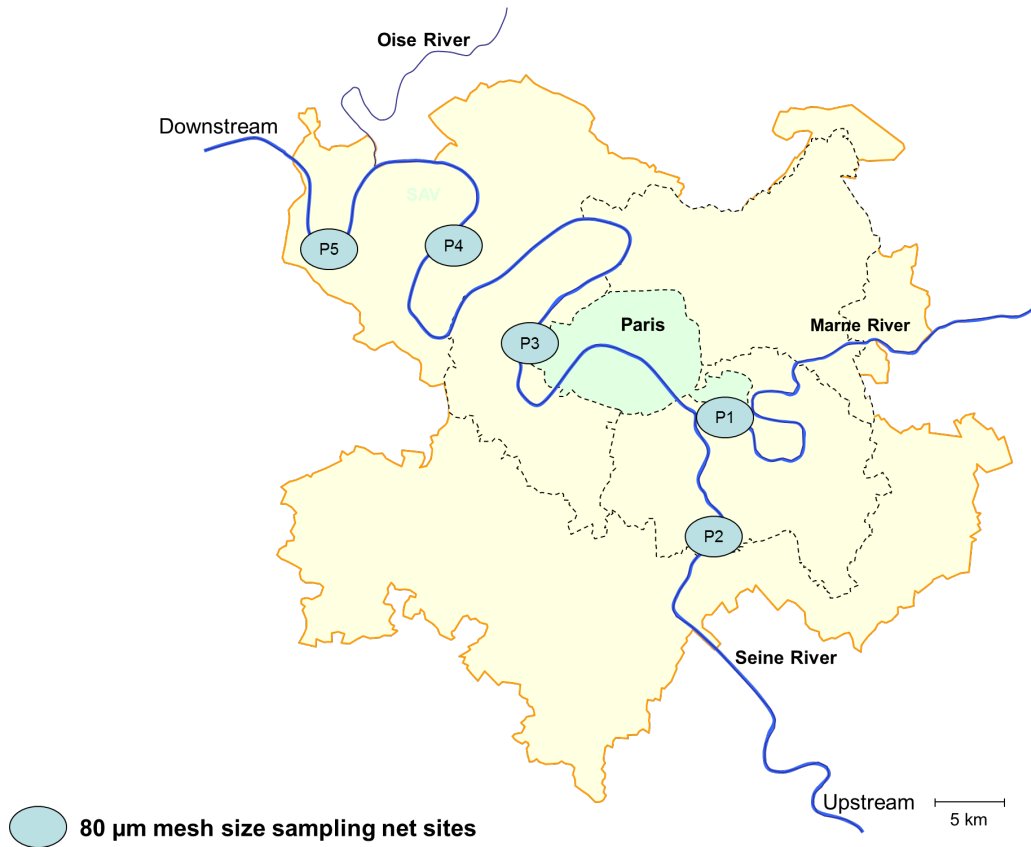


Figure 41: Location of the sites sampled during the monthly monitoring with the 80 μm mesh size net.

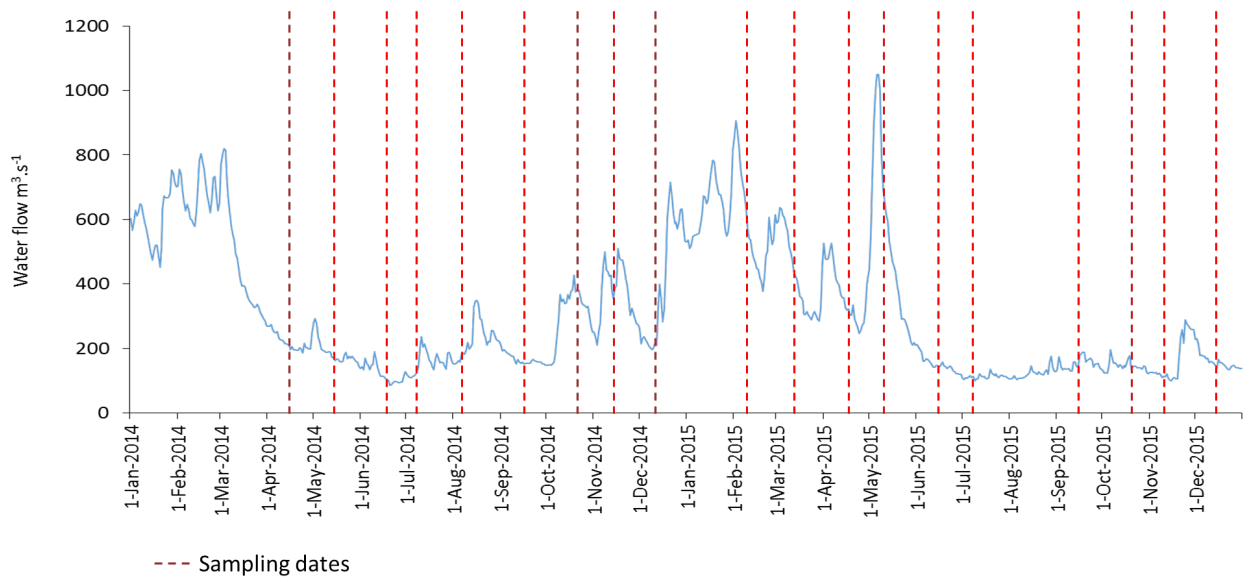


Figure 42: The water flow of the Seine River at the location of Pont d'Austerlitz with the representation of the dates of sampling during monitoring.

2. Fiber description

Fibers of various colors were observed, with a strong predominance of blue fibers. The mean diameter of these fibers was 25 μm , yet it could vary between 5 and 100 μm . The length dimension distribution follows the same decreasing pattern observed in the various urban compartments investigated in the previous chapter, with the [250-450 μm] fraction being the most abundant (Figure 43). This proportion decreases towards the larger size ranges. The smallest size range of [50-250 μm] contains fewer fibers, a finding that may be correlated with the fact that some of the fibers easily pass through the 80- μm net.

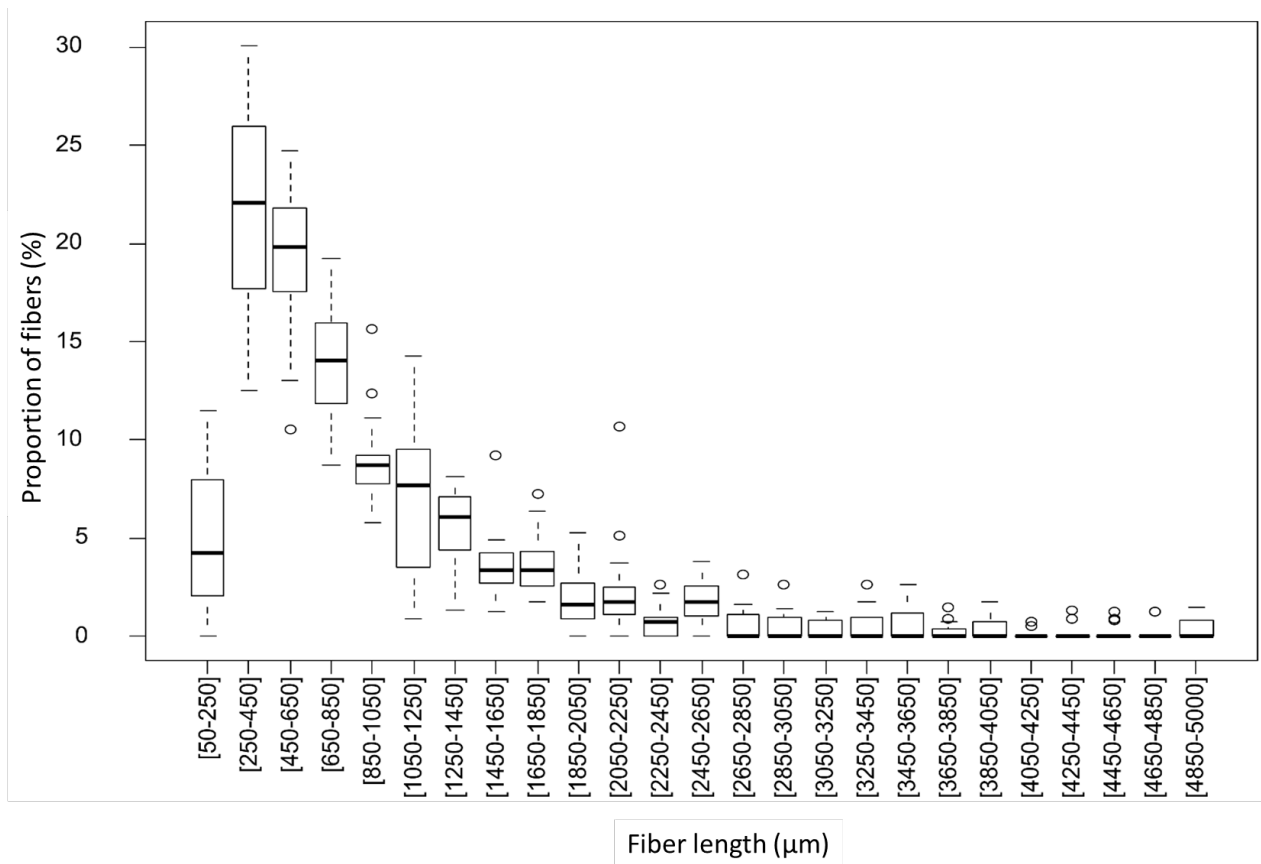


Figure 43: Size length distribution of fibers in river samples (based on $n=15$ samples and 1664 measured fibers). Boxplots are plotted from bottom to top with: [Lower quartile - $1.5 \times$ Interquartile range], [Lower quartile], [Median], [Upper quartile], [Upper quartile + $1.5 \times$ Interquartile range]. Outliers are displayed as isolated points.

3. Short-term temporal variability

During the first sampling campaign, concentrations varied between 38.2 and 101.6 fibers.m⁻³ with a mean concentration of 66.2 fibers.m⁻³ (Figure 44). The coefficient of variation equals approx. 45% - with n= 6). This variability appears to be particularly high, resulting perhaps from the variations in concentrations on the surface water due to irregular water currents, microplastic inputs and water velocities. However, it could also be due to the short sampling duration.

Accordingly, the net was deployed three times longer during the second campaign (3 minutes vs. 1 minute), leading to concentrations ranging between 18.7 and 38.6 fibers.m⁻³, with a mean of 30.4 fibers.m⁻³. The coefficient of variation dropped to 26% (n=6).

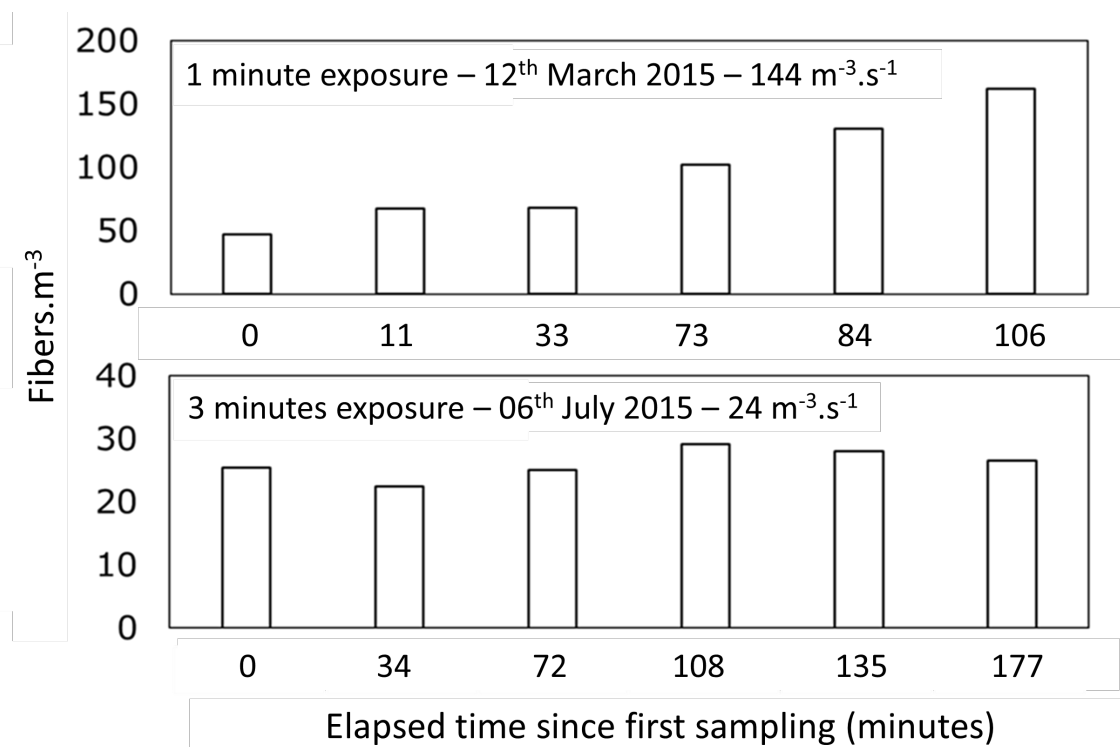


Figure 44: Short-term variability of microplastics during two campaigns carried out respectively during two and three hours.

4. *Spatial variability through the section*

Triplicates of microplastic samples in the surface-middle displayed concentrations of 16.8 - 21.3 - 24.7 fibers.m⁻³ (Figure 45), with higher concentrations on the right and left banks at 52.4 - 61.0 - 87.7 fibers.m⁻³ on the left bank and 32.1 - 34.8 - 46.4 fibers.m⁻³ on the right bank. The coefficient of variation among the nine 3-minute surface samplings equals approx. 53%, which is twice the coefficient of variation derived from the second campaign of short-term temporal variability. This finding indicates a potential difference in concentration between the middle of the watercourse and its banks. In knowing that this campaign was conducted under the same conditions (3-minute samplings within 3 hours), the level of sampling precision and short-term temporal variability do not, on their own, explain the observed fluctuations.

The higher concentrations observed near the banks might be related to the effect of intense river traffic within the Paris Metropolitan Area. It can in fact be visually observed that a boat passing generates waves that drive macroplastics and floating debris towards the banks. Similar behavior could be expected for microplastics. Lower water velocity near the banks might also explain this difference.

Concentrations of 19.0 - 20.2 - 28.2 fibers.m⁻³ were found at a 1-m depth and 13.7 - 16.9 - 19.1 fibers.m⁻³ at a depth of 2 m. In considering the nine samples collected on the vertical in the middle of the section at all three depths, a coefficient of variation of 21% was found, thus indicating that vertical variability is more than twice the lateral variability. Floating nets are widely used, like in marine environments. While it can easily be considered in marine water that fibers and microplastics float near the surface, complicated dynamics and current conditions govern their distribution through the water section in rivers. The absence of vertical homogeneity is probably caused by the turbulence factor in the river, as well as by the fact that density is higher in freshwater than in a marine environment. Boat traffic also contributes, to some extent, to the presence of turbulence.

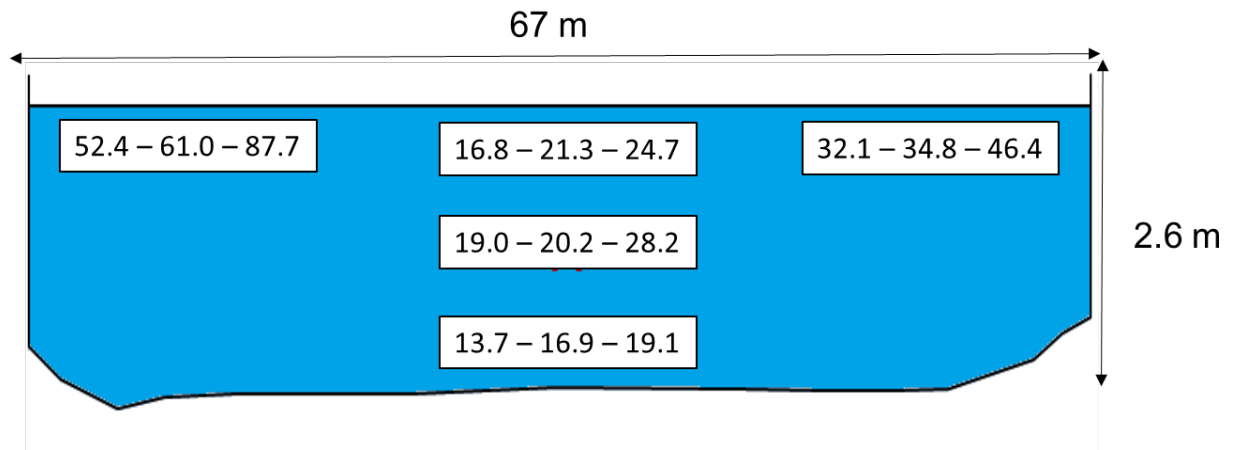


Figure 45: Concentration of fibers in all the 5 sampled points expressed as fibers.m⁻³.

5. Monitoring in the Seine and Marne Rivers

Concentrations through the year in the Marne River (P1) are between 5.7 to 398.0 fibers.m⁻³ corresponding to a mean concentration of 100.6 ± 99.9 fibers.m⁻³ (mean ± standard deviation). From the upstream to the downstream points, the observed concentrations are 48.5 ± 98.5 fibers.m⁻³ (P2), 27.9 ± 26.3 fibers.m⁻³ (P3), 27.9 ± 40.3 fibers.m⁻³ (P4) and 22.1 ± 25.3 fibers.m⁻³ (P5). Detailed results are displayed below (Figure 46).

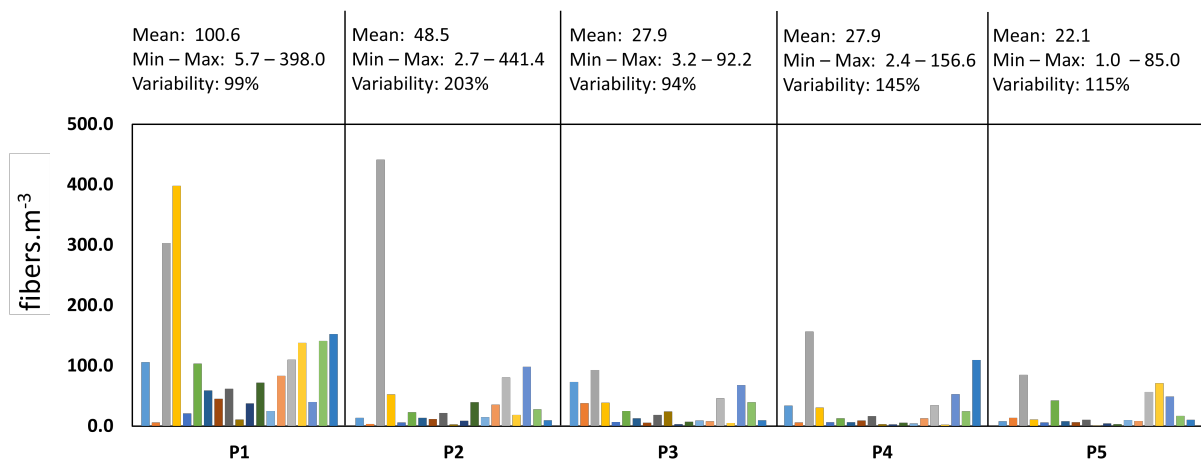


Figure 46: Concentrations obtained for the five sites during monitoring of freshwater.

The coefficient of variation lies between 94% and 203%, which is greater than the short-term temporal variability, which could suggest that even if minimal, small variations can occur throughout the year. Variations seem to occur in a similar manner across the various sites. When verifying the pairwise correlation between sites (Figure 47), the Spearman's rank correlation coefficients confirm that the various sites present correlated concentration levels (except between P1 and P3), which could indicate that global factors varying equally for all sites are more likely to affect concentrations than local or one-time factors. The variations in diffusive inputs or seasonal changes might be the cause. A correlation with river flow variations could also be suspected.

The correlation coefficients (R^2) between water flows and concentrations at the different sites equal between 0.09 and 0.24. No clear correlation could be highlighted. A tendency for fiber levels to always remain low during high water flow periods can nonetheless be observed here. During low water flow periods, the levels vary to a much greater extent and could be

influenced by different parameters, such as fiber input, either from singular sources (WWTP, CSO), diffusive sources (atmospheric fallout) or a possible re-suspension of fibers from the sediments.

Regarding spatial differences, concentrations at the five points exhibit a significant overall discrepancy according to a Kruskal-Wallis test ($p\text{-value} < 10^{-3}$). Pairwise comparisons using a Mann-Whitney test (Figure 47) show this difference to be solely due to site P1, which presents levels significantly different from all others. It would appear in fact that higher concentrations are observed at the first site (P1) (Figure 48), which is the only one located in the Marne River. This result is consistent with the pattern noted above, i.e. showing higher levels under low water flow conditions. We still lack the knowledge to date and explain such a difference.

| Mann-Whitney pairwise comparisons: | | | | | |
|------------------------------------|----|--------|--------|--------|--------|
| | P1 | P2 | P3 | P4 | P5 |
| P1 | | 0.0032 | 0.0011 | 0.0006 | 0.0002 |
| P2 | | | 0.7043 | 0.2673 | 0.1526 |
| P3 | | | | 0.3069 | 0.4655 |
| P4 | | | | | 0.9534 |
| P5 | | | | | |

| Rs Spearman test: | | | | | |
|-------------------|--------|--------|--------|--------|--------|
| | P1 | P2 | P3 | P4 | P5 |
| P1 | | 0.0047 | 0.1473 | 0.0075 | 0.0141 |
| P2 | 0.6193 | | 0.0388 | 0.0127 | 0.0072 |
| P3 | 0.3456 | 0.4772 | | 0.0006 | 0.0196 |
| P4 | 0.5930 | 0.5597 | 0.7140 | | 0.0286 |
| P5 | 0.5526 | 0.5947 | 0.5298 | 0.5018 | |

| | | | | | |
|--|--|--|--|--|---------|
| | | | | | R_2 |
| | | | | | P-value |

Figure 47: Results of statistic tests for comparison and correlation between sites.

Given the various potential fiber inputs located between the sites, the fact that levels are not significantly different from upstream to downstream does not seem intuitive. Between P2 and P5, two confluents of the Seine (Marne and Oise Rivers) are encountered, along with three wastewater treatment plant outfalls (*Seine Amont*, *Seine Centre* and *Seine Aval*), including the

largest one in France, various CSO disposals and the densely-populated city of Paris. Sinks to counterbalance these inputs could explain the fact that similar concentration levels are found upstream and downstream of Paris. A major role related to fiber sedimentation and deposition on the banks would be expected. In recognizing the short time frame required to transport particles from the upstream point downstream (an estimated 72 hours between P2 and P5, based on average water velocities), degradation was not considered to be a plausible explanation.

Suspended solids were analyzed during each campaign; no correlation appears between suspended solid levels and fiber concentration levels even though both are particulates. The correlation coefficient R^2 for all sites reaches 0.1.

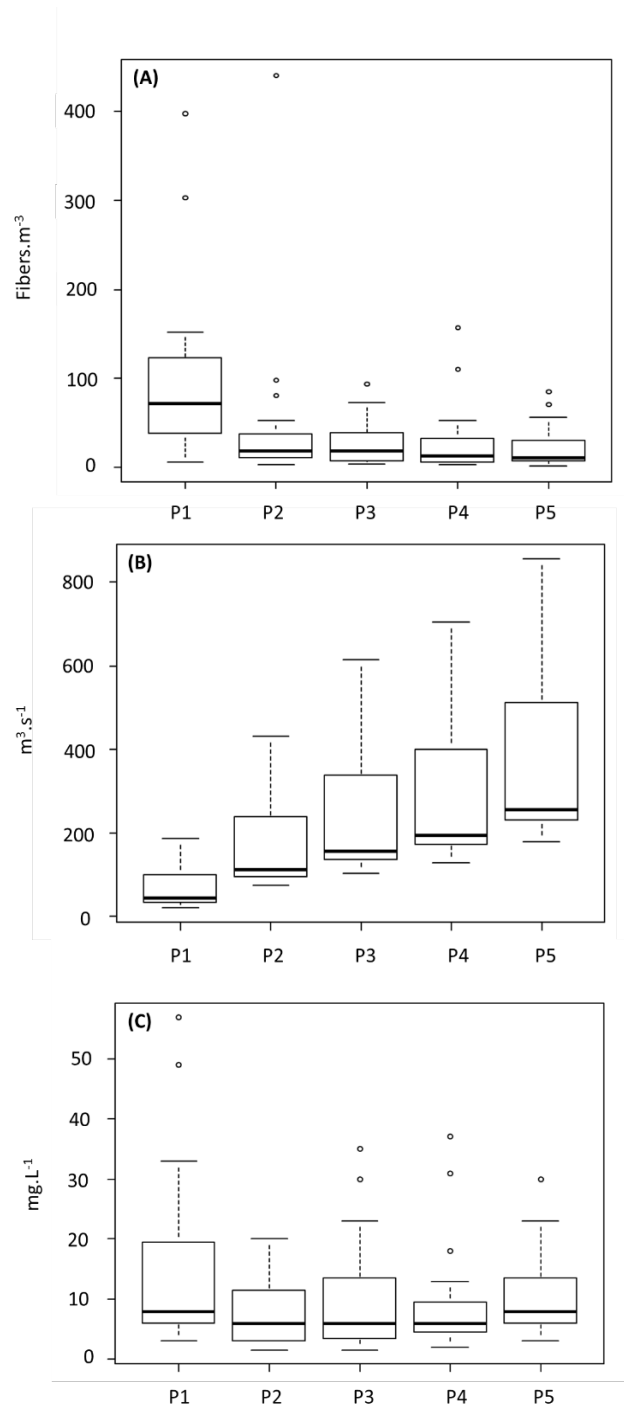


Figure 48: (A) Concentration of fibers (B) River water flow (C) suspended matter levels.

6. *Chemical characterization of the fibers*

A total of just 25 fibers were selected at random and identified in order to estimate the amount that could contain synthetic fibers among the counted fibers (Figure 49). Spectra showed a correspondence for 15 of the fibers with rayon and 1 fiber with cotton. This correspondence may be questioned since the rayon and cotton spectra are very similar. The remaining fibers (9 fibers corresponding to 65%) are all synthetic. Five of these fibers correspond to PET, while two correspond to PP and one to PA. The last fiber is a PET-PUR blend. PET is the most used polymer for man-made fibers.

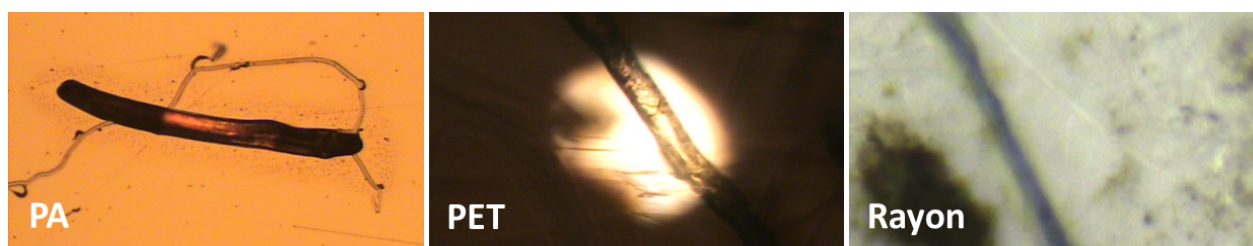


Figure 49: Example of fibers identified with the FTIR microspectroscopy.

7. Fiber flux estimations

7.1 Estimating a fiber flux according to surface-middle

Because all sampling during the monthly monitoring campaign were unique and over the surface-middle of the river, it is important before attempting a flux estimation to assess the potential errors induced by short-term temporal and spatial variabilities. The flux of fibers is estimated by multiplying the river water flow by the fiber concentration. Based on the spatial variability determined throughout the section, fluxes were estimated based on three different theories (Figure 50):

- Hypothesis A: By only taking into account the concentration found on the surface-middle point ($n=3$) and considering water flow over the entire section, a flux of 1,445 fibers. s^{-1} has been estimated.
- Hypothesis B: The horizontal variability is taken into account. All three points on the surface are considered ($n=3*3$). The river section is divided into three sections with perpendicular bisectors. The measured water velocity and fiber concentration at each point are combined to estimate the fiber flux on each section. By summing the three fluxes, a global fiber flux of 2,421 fibers. s^{-1} is obtained. In conclusion, neglecting the horizontal variability induced in this case leads to an underestimation of 40%.
- Hypothesis C: The vertical variability is taken into account. By using the same method as in the previous hypothesis with all the middle points, a global fiber flux of 1,384 fibers. s^{-1} is derived. This figure shows that if vertical variability is neglected, a small overestimation of only 4% is introduced. This error is lower than that induced by the short-term temporal and horizontal variabilities.

Since the fiber concentration and water velocities in the right and left bank vertical profiles were not measured, the hypothesis that takes into account both horizontal and vertical variabilities was not adopted herein. Let's keep in mind that this test has only been applied to the low-depth case (2.6 m) and still needs to be verified for wider and deeper rivers under different current conditions. These approximations should be kept in mind when interpreting the fluxes presented in the next section.

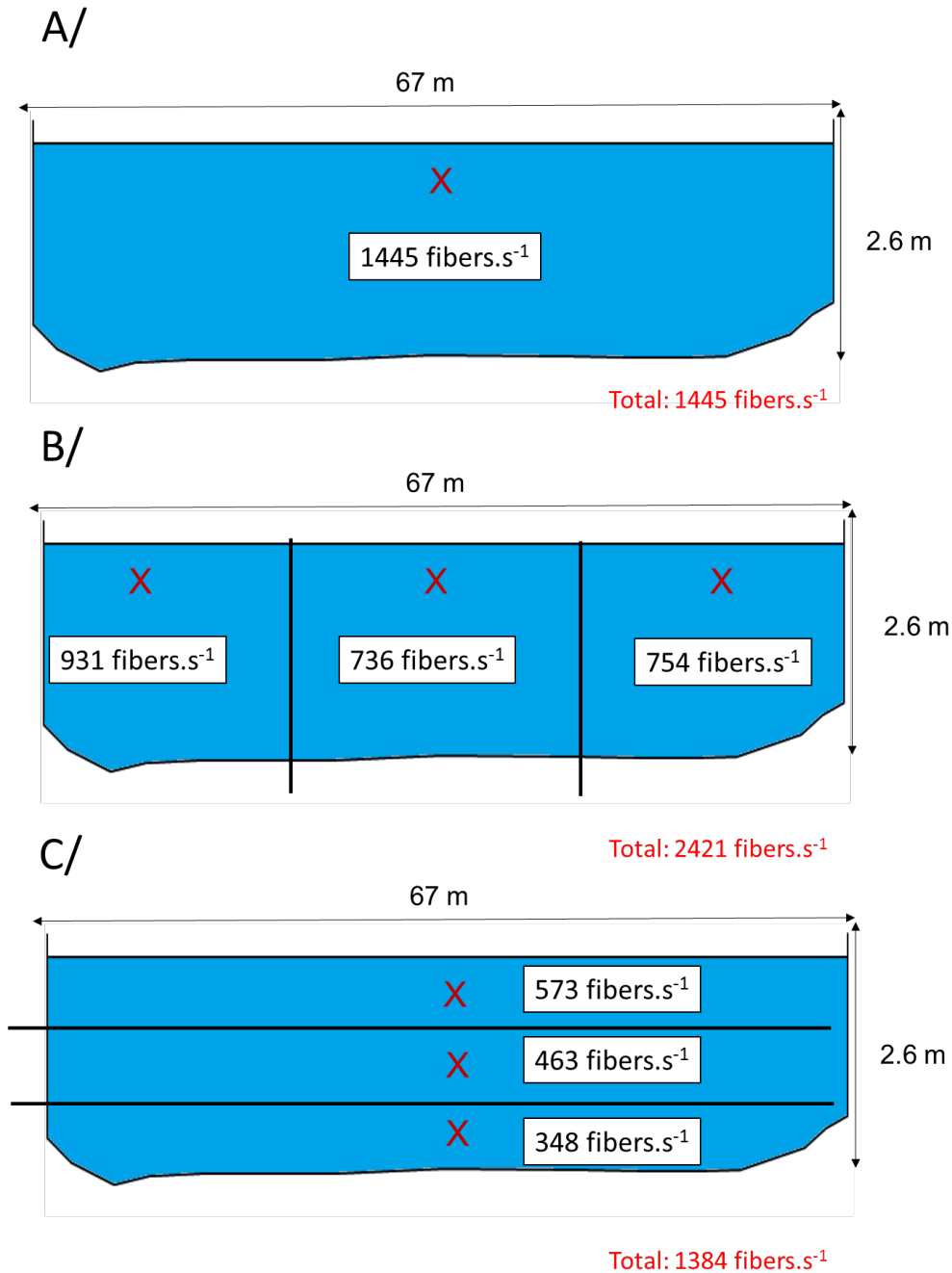


Figure 50: Fluxes estimations by considering different point on the water section.

7.2 Annual flux for the Seine River

It is to assess the annual fiber fluxes in the Seine River using the 19 individual fluxes calculated at each site; results are presented in Figure 51. Both the upstream point (P2) and downstream point (P5) display nearly similar fluxes. The increase between these two stations is only 6%, i.e. much smaller than the uncertainty induced by the short-term variability discussed above.

Consequently, as regards the fibers, it seems that the impact generated by the Paris Metropolitan Area cannot be distinguished. The current state of knowledge does not provide an understanding or explanation of this non-increasing pattern. It can be assumed that in the case of the Paris Metropolitan Area, sinks and sources reveal similar levels.

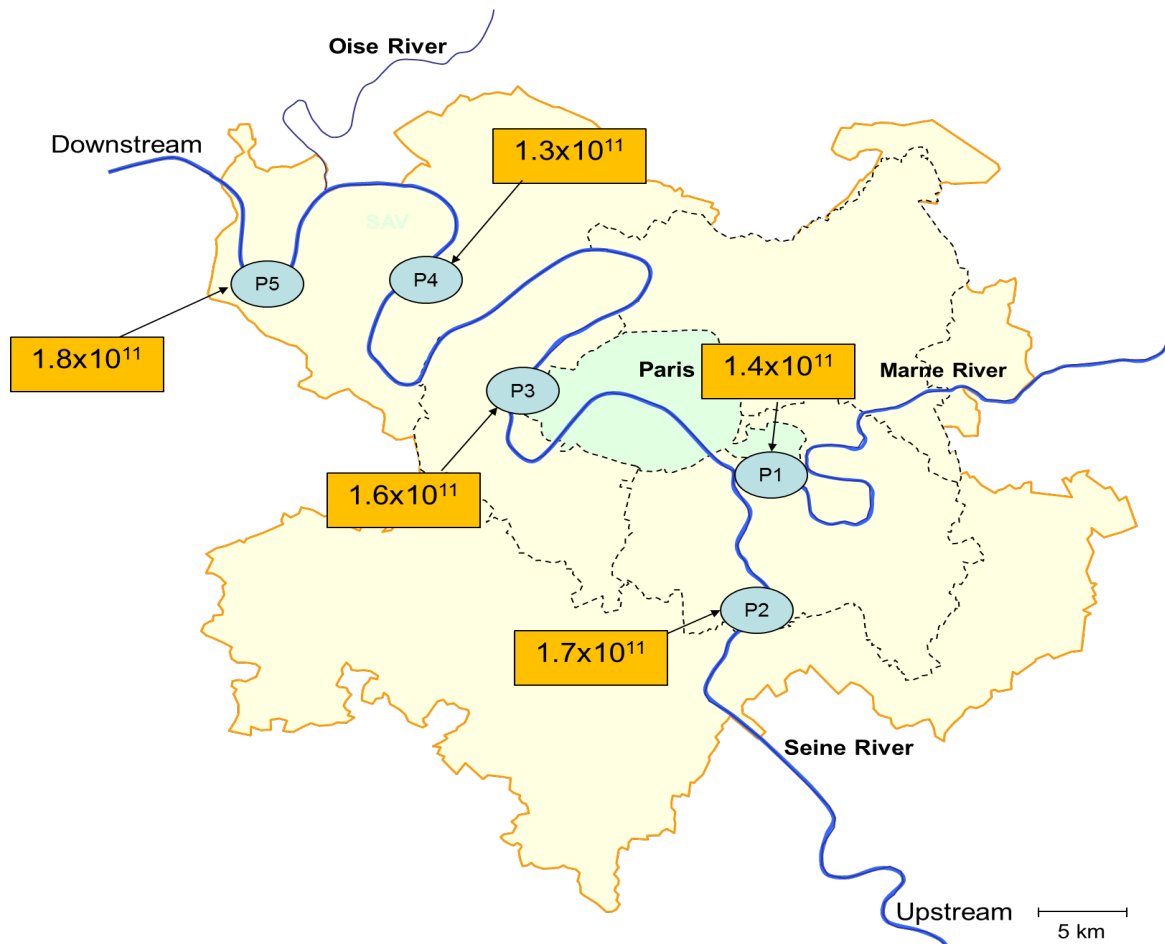


Figure 51: The number of total fibers that flow in each site during one year. These results are extrapolated from the monthly monitoring samplings.

The minimum and maximum estimated fluxes for site P5 are respectively 2.8×10^{10} and 6.1×10^{11} fibers per year, with a mean value of 1.8×10^{11} . Given the hypothesis that 65% of fibers are synthetic, it is approximated that between 1.8×10^{10} and 4.0×10^{11} microplastic fibers flow into this site per year. According to the same methodology described in the previous chapter, it is estimated that a synthetic fiber mass of between 0.01 and 0.34 metric tons flows per year.

II. Fragments: characterization, concentrations, fluxes

1. *Sampling approach*

Two different types of nets were used to sample with a 330- μm mesh size:

- A plankton net was designed and used in a similar way as described previously for the 80- μm net; it was deployed from bridges and coupled with a current meter. The only difference consisted of the fact that this one was larger with a sampling surface area of approx. 1,962 cm^2 .
- A manta trawl was also deployed by means of towing by a motorboat in the upstream direction for 10 minutes over distances of between 0.5 and 1.5 km. The sampling surface area of the manta trawl is roughly 1,350 cm^2 . After towing, the trawl was rinsed from the outside with river water. This method led to collecting a sizable amount of plant/vegetal debris. The use of a 2-mm sieve was therefore required in order to remove this debris, which wound up considerably increasing the volumes and potentially hindering the purification step. The fraction retained by the sieve was rinsed and sorted to keep just the plastic debris while the rest was discarded. The entire fraction passing the sieve was kept and taken to the laboratory for treatment.

1.1 Static sampling using 300 μm mesh plankton net

Two campaigns with two distinct purposes were carried out using the plankton net:

- On 24th March 2016, a campaign was held at site P1. Three samples were extracted with the net deployed for 5, 15 and 20 minutes. This campaign was mainly intended to verify whether the results obtained with the various sampled volumes and on the same day were of the same order of magnitude. The 20-minute sample had to be discarded because the high level of suspended solids interfered with sample treatment, making it impossible to filter and observe. In 5 minutes, the 32- m^3 volume had been sampled vs. 89 m^3 in 15 minutes.
- A second campaign was carried out at the 5 monitoring sites (P1 to P5) on 4th July 2016. The net was deployed for 5 minutes on each site, and volumes of between 40 and 73

m³ were sampled. This campaign was intended to verify whether the upstream-to-downstream evolution of fragments could be easily highlighted.

1.2 Dynamic sampling using a 330 µm manta trawl

Five different campaigns were conducted with the manta trawl on the various sites (Figure 52). Volumes between 70 and 200 m³ were sampled. One of the campaigns was conducted on the site M1 which is upstream the Paris agglomeration. Sites M2 and M3 are located respectively upstream and downstream the WWTP of Seine Centre while M3 and M4 are located respectively upstream and downstream the large WWTP of Seine Aval.

| | M1 | M2 | M3 | M4 |
|---------------------------------|----|----|----|----|
| 17 th July 2014 | | ✓ | ✓ | ✓ |
| 9 th October 2014 | | ✓ | ✓ | |
| 17 th September 2015 | | | ✓ | ✓ |
| 8 th October 2015 | ✓ | | | |
| 14 th October 2015 | | | ✓ | ✓ |

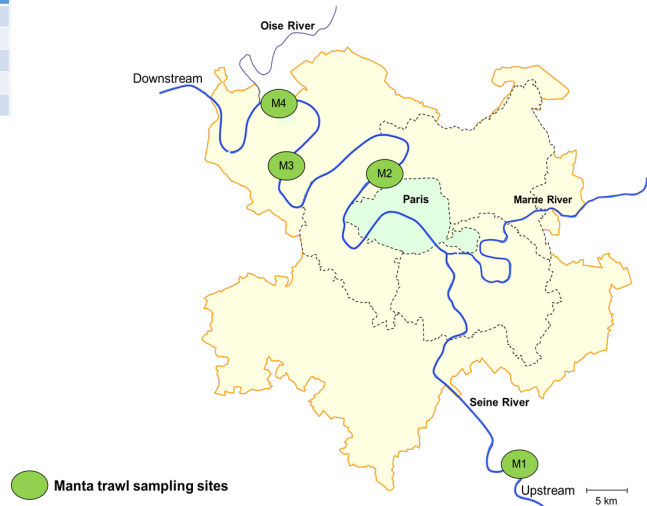


Figure 52: Location of the four sites sampled with the manta trawl and the various dates of sampling.

2. *Fragments description*

As for fibers, many different colors were found for fragments. These non-fibrous microplastics presented various shapes: irregular shapes, regular shapes (rectangular, triangular, etc.), lines (i.e. 1D fragments yet larger than fibers), ovals, films, foams and spheres. 75% of the fragments identified were blue; yellow, red, gray, purple, brown, pink and black particles could also be detected.

The apparent area of the fragments was measured (Figure 53); this measurement corresponded to the surface area of the projected perimeter of each fragment. The fragments were categorized by this area. The upper limit of the smallest range was $50,000 \mu\text{m}^2$, while the largest range encompassed fragments larger than $500,000 \mu\text{m}^2$, which could correspond to a 2.5 mm x 2 mm rectangle.

40% of the fragments had an area of less than $50,000 \mu\text{m}^2$, and the number of fragments seemed to decrease with area. However, larger fragments significantly contributed to the total area. Though the largest fragments only accounted for 7% of the total number of fragments, their cumulative area actually represented 45% of the total cumulative area. This finding indicates that the largest particles are also predominant as regards fragment volumes; therefore, they would likely also account for the greatest share of both mass concentrations and fluxes. Observing the sizes of particles in freshwater is important because the dynamics experienced depend in part on size.

These fragments were extracted with a thin pointed tweezers in order to estimate thickness. As opposed to the area, only very rough estimates could be drawn. Fragment thickness was estimated at between 10 and 100 μm , but this value lacked accuracy; methods must be developed to allow estimating the thicknesses of the smallest particles.

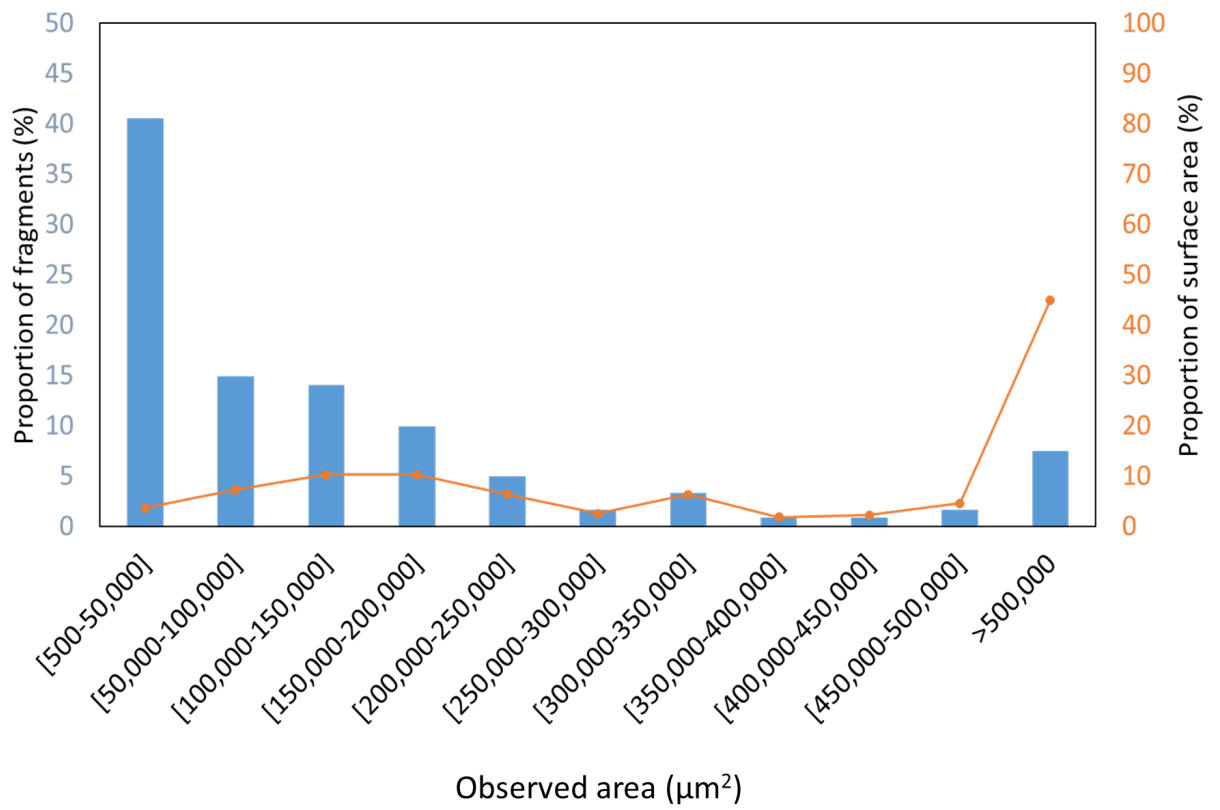


Figure 53: The area distribution of fragments based on n=15 surface water samples.

3. Concentration of fragments collected with static sampling

During the first campaign, two samplings were carried out, with the respectively a duration of 5 minutes and 15 minutes. The 5-minute sampling showed a concentration of 1.42 fragments.m⁻³, while the 15-minute protocol reported 1.37 fragments.m⁻³. These values, which are very close, indicate an absence of clogging and a potentially low short-term variability for fragments compared with fibers.

During these five-site campaigns, the P1 site revealed a concentration of 1.16 fragments.m⁻³, which is slightly lower but on the same order of magnitude as that observed in the previous campaign. From P2 to P5, the observed concentrations were respectively 1.35, 0.88, 1.32 and 1.57 fragments.m⁻³. While no clear increasing pattern exists, the concentration level observed at the downstream point P5 is higher than that found at upstream point P2; this result should be interpreted with caution given that only one campaign was conducted on these four sites using the 330- μ m mesh size net.

4. Dynamic sampling using a 330 μm manta trawl

The concentration levels recorded for all campaigns are listed in Table 16, ranging from 0.10 fragments. m^{-3} at site M4 to 0.28 fragments. m^{-3} at M1, with only slight variations depending on the campaign and site. Moreover, these results are lower by one order of magnitude than what was observed in the plankton net samples, owing perhaps to an array of methodological issues. For instance, in order for the boat not to lose balance, the manta trawl had to be towed behind the boat over a small distance, thus altering the sample due to previous boat runs, which could induce increased turbulence and smaller sampled volumes.

In this context, any definitive interpretation of these results would be unwise. Nevertheless, they have been presented here to raise awareness of this methodological issue regarding river sampling. In many rivers, only small boats can in fact navigate; however, as in our case, large trawls cannot be towed too far behind the boat or beside the boat out of fear the boat loses its balance. Consequently, when larger boats are infeasible, other devices should be designed. Much smaller manta trawls could be towed or stationary nets could be deployed.

Table 16: The level concentrations of fragments for each sample expressed as fragments. m^{-3} .

| | M1 | M2 | M3 | M4 |
|---------------------------------------|-------------|-------------|-------------|-------------|
| 17th July 2014 | | 0.16 | 0.16 | 0.28 |
| 09th October 2014 | | 0.15 | 0.17 | |
| 17th September 2015 | | | 0.17 | 0.10 |
| 08th October 2015 | 0.29 | | | |
| 14th October 2015 | | | 0.25 | 0.12 |

5. Chemical characterization

Among the 38 fragments characterized, one presented a non-identified spectrum and most likely corresponded to a natural organic particle. All the remaining fragments were microplastics. PE accounted for 50% of the analyzed fragments (Figure 54), which is consistent with the polymer demands provided in Chapter 1. Moreover, PE is widely used in disposable products that would more likely end up in the environment. PP is the second most common polymer at 29%; it is also the second most widely used polymer in Europe and mainly contained in disposable products like packaging. The remaining particles consisted of PS and PET, both of which are also heavily used. One of the particles found was a copolymer of PE and PP.

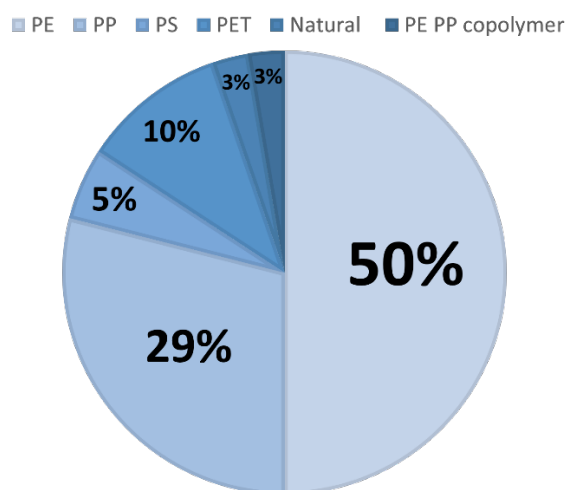


Figure 54: Proportion of polymer nature for n=38 fragments.

III. Fibers and fragments comparison

This study has highlighted a large discrepancy in the concentration levels between fibers and fragments (Figure 55). The mean fiber concentration across all 95 samples extracted equals around 45 fibers.m^{-3} , while the mean fragment concentration when considering both methods is approx. $0.54 \text{ fragments.m}^{-3}$. Consequently, the use of two distinct sampling methods for fibers and fragments seems especially pertinent. Regardless of whether fiber analysis requires use of a small mesh size, higher sample volumes are still mandatory to collect other shapes of microplastics.

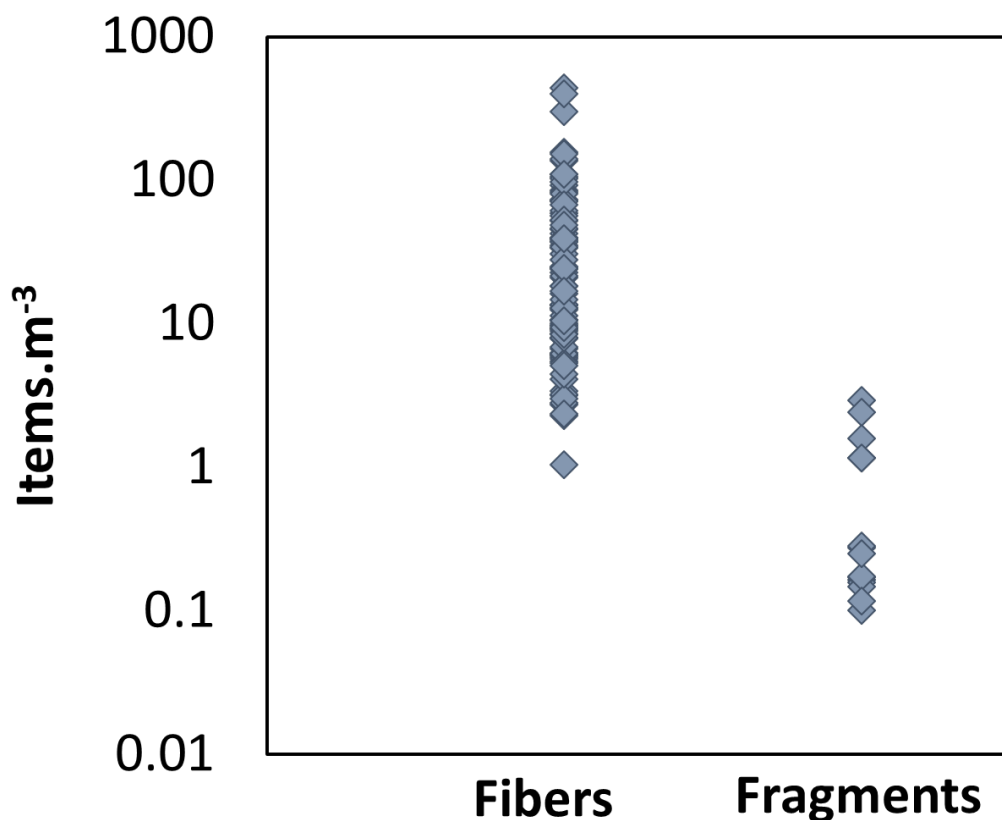


Figure 55: The concentration of fibers and fragments based on all the samplings conducted in this study. The term items is here used as it can be replaced accordingly with either fibers or fragments.

By setting for fibers a mean length ($973 \mu\text{m}$) and a diameter ($25 \mu\text{m}$) and for fragments a mean area ($168,000 \mu\text{m}^2$) and a roughly estimated thickness ($35 \mu\text{m}$), the volumes of a typical particle can be approximated for each shape. Combined with microplastic proportions and

polymer densities deduced from the characterization step, the various mass concentrations have been approximated.

The mean concentration for synthetic fibers was estimated at $2.10^{-5} \text{ g.m}^{-3}$ vs. $3.10^{-6} \text{ g.m}^{-3}$ for fragments. Due to the limited amount of data, the fragment mass flux could not be estimated. With this result however, it seems that even if a fragment is on average larger than a fiber, fragment mass fluxes would still be an order of magnitude smaller than fiber mass fluxes.

IV. Comparison with Ho Chi Minh City case

A sampling campaign was conducted on the Saigon River and its adjoining canals on 10th and 11th December 2015 (Figure 56) in Ho Chi Minh City (HCMC). After a preliminary study on two samples (not presented here), it was considered that the fiber concentration level in HCMC is high enough to be estimated on small bulk water samples. Hence, 300 ml of bulk water were collected using a bucket, after thorough homogenization, in order to quantify fibers. To sample a higher volume of water as a means of concentrating the fragments, a 330- μm sized zooplankton net was deployed for 60 seconds. The same sampling method was followed as for the plankton nets used in the Paris area (coupled with a General Oceanic current-meter).

Net samples and bulk samples were collected in Kenh Te (3), Tau Hu (4) and Lo Gom (5). For Site 1, which lies on the Saigon River, both middle (from bridge) and riverside were considered. The water velocity varied between 0.01 and 0.33 $\text{m}\cdot\text{s}^{-1}$ on the canals and in the Saigon River for riverside samples, while it was 1.41 $\text{m}\cdot\text{s}^{-1}$ in the middle of the Saigon River.

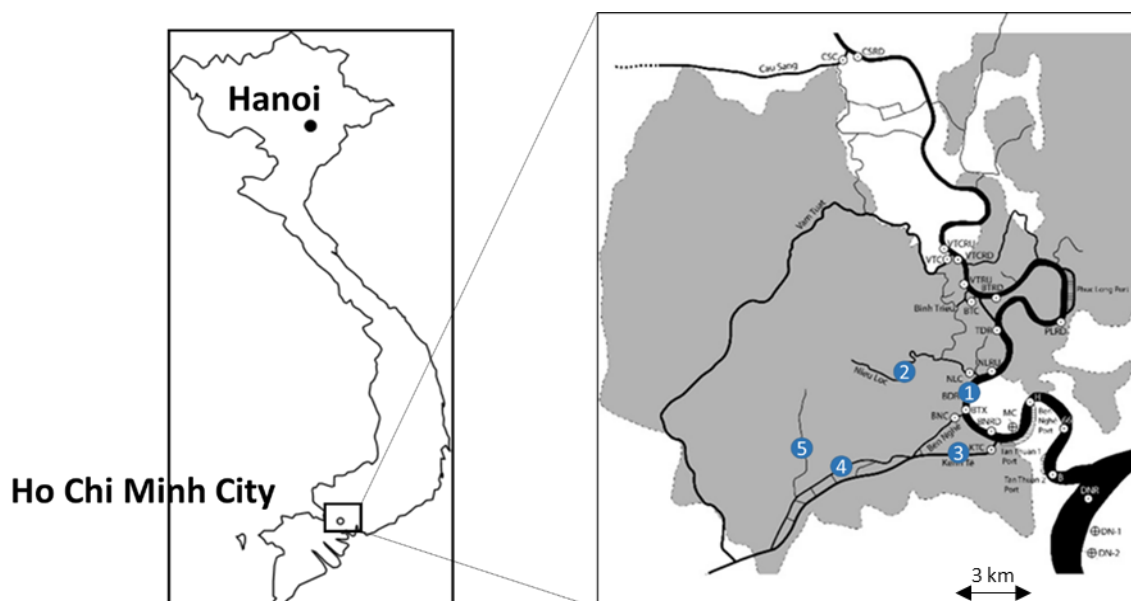


Figure 56: Sampling sites; 1: Bach Dang, 2: Nhieu Loc - Thi Nghe, 3: Kenh Te, 4: Tau Hu, 5: Lo Gom.

1. Concentration of fibers

Bulk samples were collected only in the Tau Hu, Kenh Te and Lo Gom canals. Fibers were therefore only counted and measured on these samples. While only considered on bulk samples, fibers were found in various colors and lengths. Their size distribution is similar to that discovered in Paris area rivers.

Fibers were found in very high concentrations in the canals: 270×10^3 fibers.m⁻³ in Tau Hu, 466×10^3 fibers.m⁻³ in Lo Gom, and 519×10^3 fibers.m⁻³ in Kenh Te. These values are comparable to the fiber concentrations recorded in raw wastewater in Paris (Chapter 4) and much higher than concentrations measured in the Seine and Marne Rivers (by three orders of magnitude). This finding is not surprising given the very dense population and slum areas located adjacent to the canals. High fiber concentrations might indeed be correlated with the high proportion of untreated wastewater discharged into the canal plus the lack of sewage for a large share of the population. In contrast, the use of washing machines is not as common in Vietnam as in more developed countries. Hand-washing might also discharge a certain amount of fibers. Moreover, several textile industries are located in HCMC, and their discharges could provide a major source of fiber contamination.

The high concentrations and variations across these three canals could be explained by the different dynamics of the waterways. Due to tidal effects, stagnation rates rise considerably, thus resulting in longer residence times. At the time of sampling, the water in Lo Gom seemed to be more stagnant than in the other canals, which might have contributed to a one-off fiber accumulation. The higher concentrations in Kenh Te may be due to the inputs of its many tributaries, including Tau Hu, which drain the city center and are likely to import significant amounts of fibers from wastewater discharges.

2. Concentration of fragments

Net samples were collected at every sampling point, allowing for the observation and measurement of fragments in the Saigon River and all canals. Most fragments featured an irregular shape, with blue being the prevailing color. The shapes found were generally similar to what was observed in Paris, although the expectation of finding microbeads and spherical particles never materialized. These microplastics were also reported to be absent in the Yangtze River by another study (Zhang *et al.*, 2015), while microbeads were indeed detected on the Rhine River in Germany (Mani *et al.*, 2015). This Asian/European difference could be attributed to a difference in consumer habits or in cosmetics composition, since microbeads are mainly present in facial cleansers (Napper *et al.*, 2015)

Table 17: Fragments concentrations in the Saigon River and the canals.

| | | Fragments.m ⁻³ |
|--------------|---------------|---------------------------|
| Saigon River | Bridge (1) | 2.96 |
| | Riverside (1) | 9.65 |
| Canals | Nhieu Loc (2) | 19.50 |
| | Tau Hu (4) | 22.77 |
| | Kenh Te (3) | 142.21 |
| | Lo Gom (5) | 222.97 |

Fragment concentrations vary from 3 fragments.m⁻³ in the Saigon River to 223 fragments.m⁻³ in the canals (Table 17). As for fibers, Lo Gom and Kenh Te exhibit higher concentrations than Nhieu Loc, probably due to the water stagnation and the tributaries inputs respectively. Indeed, Nhieu Loc is a smaller canal with fewer tributaries.

The dilution factor could explain the difference between the canals and the Saigon River samples. The difference between the two samples on the Saigon River can be explained by

the fact that one of the samplings was carried out from a bridge (at the middle of the water section) while the other was done from the riverside. We showed previously that fibers can accumulate close to the shore. A similar pattern could be expected for fragments. If we take the sample collected at the middle of the water section we find a concentration level (2.96 fibers.m⁻³) in the same order of magnitude as the samples collected in the Paris agglomeration with the same net and the same methodology.

V. Conclusions

This chapter has investigated fiber and plastic fragment contaminations in Paris freshwater sources. A dual approach was implemented in order to sample different volumes depending on concentration levels.

Regarding the fibers, smaller volumes were sampled with an 80- μm mesh size net to limit fiber loss. The temporal variation campaigns proved that deploying the net for a longer time period (3 minutes vs. 1 minute) serves to reduce variability between consecutive samples. However, even though sampling higher volumes increases representativeness, the presence of clogging actually limits representativeness.

Fiber variability throughout the water section was assessed, in revealing that concentrations are similar over the entire river depth while concentrations tend to rise near the banks. It was shown that vertical variability could be neglected when fluxes are being estimated yet horizontal variability exerts greater impacts.

During a lengthy monitoring campaign at 5 different sites, only small variations occurred. Concentrations varied similarly across the various sites. No direct correlation was highlighted between concentration levels and water flows. However, while concentration levels are variable during low water flows, they remain low as water flow increases. The concentration variability is therefore due in part to water flow, but also to other undetermined factors, likely related to the inputs. The annual fiber flux at each of the five sites was estimated based on monitoring results. Fluxes were similar upstream and downstream of the Paris Metropolitan Area. The impact of Paris therefore was not pronounced, and fibers did not appear to accumulate in the downstream direction. Further work is still needed to understand the various potential mechanisms and dynamics responsible for this pattern. For instance, fiber sedimentation is a subject that merits investigation.

Fragments were also studied in this chapter. Larger mesh size nets (300 μm) were introduced in order to collect larger volumes and thus a representative number of fragments. A static approach with a plankton net and a manta trawl towing procedure were both used as well. regardless of the method employed, it was shown that fragments are less concentrated than

fibers, with levels 80 times smaller on average. Fragments are less prevalent than fibers in terms of both numbers and mass fluxes.

A comparative study was conducted in HCMC, where contamination levels were shown to be much higher. The range of uses and absence of water treatment are probably responsible for this wide disparity. Though concentration levels differed substantially, the predominance of fibers was also found in HCMC. Fibrous contamination indicative of microplastics would seem to characterize urbanized areas.

Chapter 6: General conclusions, research needs and outlook



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Research on the topic of plastics in both continental and urban environments is in its infancy. Given this context, the present PhD thesis has been aimed at estimating the plastic fluxes in urban systems. Due to the innovative nature of this global approach, thesis results display a level of uncertainty and raise many questions to be addressed in future works. Consequently, a complete chapter has been devoted herein to discussing the most important findings and emphasizing the research needs for the topic of plastics in general, while providing some direct perspectives regarding this work program.

The discussion presented in this chapter will be conducted by bearing in mind the main goals that initially prompted this study. The first part intends to assemble the various fluxes calculated over the course of this thesis (Chapter 3, 4 and 5) and to deduce from them a set of primary conclusions. The second part will identify global research needs, focusing in particular on methodologies. The last part will offer the direct consequences and a number of perspectives gained from this effort.

I. Conclusions on plastic contamination and fluxes in an urban environment

1. *Mass balance of microplastics in urban hydrosystems*

Even though mass estimations of plastics are based on rough approximations, we have elected to base this discussion on mass fluxes rather than numerical fluxes. Since plastics may be fragmented and therefore continuously change in both number and size during transport in urban compartments and receiving environments, the only way to proceed with a comparison is to use the total plastics mass, which should be a conservative figure (if all sinks are considered).

It was estimated in Chapter 4 that the amount of synthetic fibers at the entries to Paris' WWTPs lies between 2 and 225 metric tons. Between 0.1 and 45 metric tons remain after treatment and are released into the environment. The fragment mass outputs have been considered to be very low and thus eliminated from the WWTP output estimations.

While the estimation of WWTP output is quite reliable, it is still difficult to produce one for the other potential sources. Atmospheric fallout, for instance, is not a direct source into natural hydrosystems. It was estimated that between 6 and 17 metric tons fall on the surface of the Paris agglomeration, yet the fraction actually reaching aquatic environments, whether directly or indirectly, has gone completely undetermined. If we approximate the surface water proportion on the Paris agglomeration area to 0.3%, we can estimate that 0.1 metric tons of microplastics fall directly on the surface water, which lies on the same order of magnitude than the WWTP output estimations. It appears therefore complicated to conclude on majors contributors. In an initial approach, only WWTP outputs have been compared here with freshwater fluxes.

For freshwater at site P5 (i.e. the site furthest downstream), it was estimated that between 0.01 and 0.34 metric tons of synthetic fibers flow annually; this estimation is of the same order of magnitude as the lower estimation for WWTP output. However, the fact that similar amounts of synthetic fibers were found on upstream sites serves to complicate any interpretation of these patterns. In this work, no flux evolution was detected from the

upstream-to-downstream sites. Fragment fluxes in freshwater were, like for WWTP output, neglected as a result of the observation in Chapter 5 that their mass concentration is much lower.

This work has provided estimations of urban microplastic inputs into freshwater and the actual amounts flowing into freshwater, yet no knowledge whatsoever has been derived regarding the sinks. A further investigation of sinks could help clarify some inconsistencies, mainly concerning the relatively low amount of synthetic fibers downstream. The most critical investigation to conduct in the future would focus on the sediment compartment. A previous work showed, by sampling, at various points along the Rhine River that microplastic concentrations increased considerably near large cities but also decreased very quickly downstream (Mani et al., 2015). For the Paris agglomeration, it is plausible that a pattern could be highlighted if we were to sample points located upstream of site P2 and downstream of site P5.

It is entirely unknown how the sediment and water cross-section interact as regards microplastics. It is already known that microplastics can accumulate in river sediments, like a previous study highlighted for the Thames River (Horton et al., 2016). Data on concentrations are however not sufficient to gain a complete understanding. The sedimentation rate, along with the potential re-suspension of microplastics from the river bottom, would need to be examined in order to develop a better understanding of the dynamics of these pollutants in riverine environments. The benthic boundary layer should also be examined to better determine the global dynamics and transport mechanisms of microplastics.

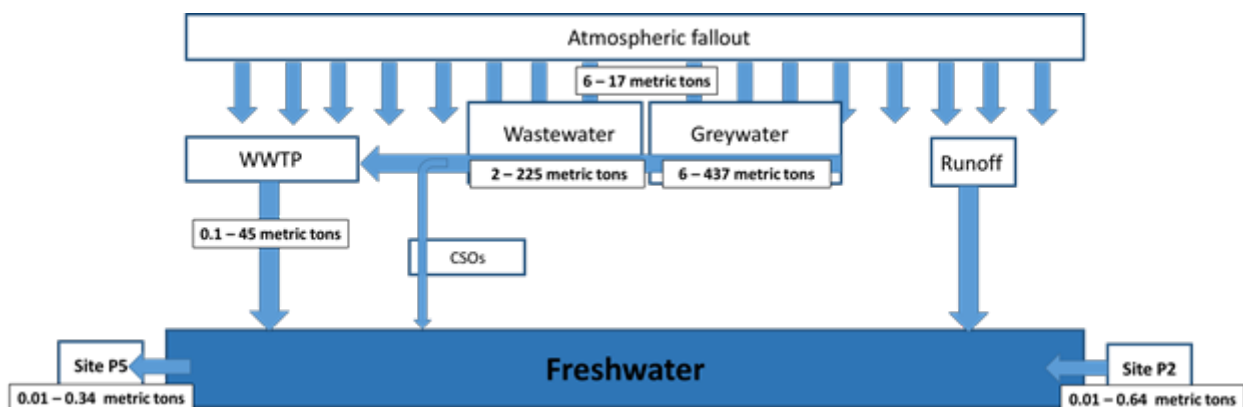


Figure 57: Microplastic fluxes upstream and downstream of Paris, plus inputs from the Paris agglomeration.

2. *Plastics fluxes in the Seine River*

In this study, macroplastics, synthetic fibers and microplastic fragments were all estimated on the Seine River. By considering all the various approaches and tests carried out in Chapter 3, the annual flux of macroplastics on the Seine River was estimated to be at least 750 metric tons (according to a theoretical approach based on SYCTOM data). When relying on the field approach alone, the annual flux would equal at least 1,000 metric tons. In all cases, macroplastics display a much higher total mass than either synthetic fibers (max. 0.34 metric tons) or microplastic fragments (a negligible fraction).

This information should help future works concentrate their efforts more effectively depending on the aim of the study. If the primary aim is to estimate plastic fluxes from the continents into the marine environment, then microplastics should be overlooked in favor of focusing on macroplastic fluxes. As discussed above, macroplastics require higher sampling volumes and a less sophisticated methodology than microplastics for their quantification. When seeking to estimate the quantity of plastics in the environment, it is quite unreasonable to take into account microplastics, especially given the continuous degrading pattern inherent in macroplastics. In fact, it is plausible to assume that within a relatively short time frame, the macroplastics quantified on the river will degrade and potentially produce in the marine environment, should they reach it, even more microplastics than the microplastic flux on its own.

While macroplastics exceed microplastics in terms of both mass and volume, microplastics are predominant in numerical terms. Microplastics thus represent a distinct topic more closely related to the ecotoxicological impact. Consequently, future work regarding microplastics in the continental environment should mainly focus on this latter aspect. For instance, fibers have already been found on the gut content of freshwater fish (Sanchez et al., 2014). Though the presence of fibers has now been confirmed in freshwater and on freshwater biota, the correlation between concentration levels and their potential impacts has yet to be determined and requires further examination.

II. Research needs in the topic of plastic pollution

1. *Estimating macroplastic fluxes*

In this thesis, various approaches have been applied to approximating the macroplastics flowing into the Seine River. The first such approach was based on a field study. In sampling macroplastics, quantifying and characterizing them are rather simple steps, whereas accurately approximating their flow in rivers appears to be a real challenge. We benefited herein from a network of previously installed booms for generating large-scale estimations. The booms however only sample floating plastics initially located near the banks or moving towards the banks. A prior work on the Thames River also found that plastic flows at the river bottom (Morritt et al., 2014). Producing an accurate overview of macroplastics in a river thus requires covering the entire water cross-section, a task that is generally impossible, especially in navigable rivers. We proceeded by extrapolating what was collected on the booms to the entire cross-section by hypothesizing a homogeneous plastic flow, which remains to be verified.

Another methodological consideration pertains to the integration time. It is actually impossible to sample all plastic passing through the water cross-section over very long periods. The booms used herein for sampling continuously collected plastics, but only a small fraction was analyzed and results were then extrapolated. The integration time required for an accurate estimation, but with a manageable amount of plastic, has yet to be evaluated.

In light of this constraint, the ideal situation would be to develop a kind of driftnet for deployment on the entire cross-section over a long period (e.g. one week) capable of collecting all the plastics passing. This proposal relates to the work carried out on the Danube River (Lechner et al., 2014), although those driftnets only covered part of the cross-section.

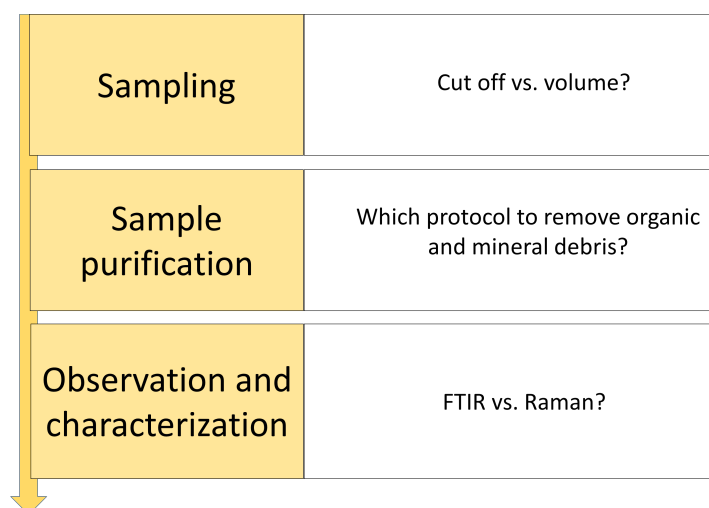
To overcome these difficulties, a second more theoretical approach was also tested. Such an approach is based on official statistical figures, provided for the most part by waste management authorities and services. The figures typically listed relate to the fraction that is well managed and remains within the waste management circuit or else reenters the circuit at a certain point (e.g. street cleaning, cleanup operations on riverbanks or lake shores, river

cleaning services with specific installations like the booms in Paris or manually like in Ho Chi Minh City). The heavily leaked fraction is inaccessible and therefore absent from the comprehensive data available. This fraction can only be approximated by means of extensive hypothesis.

In this context, even though macroplastics do not raise the same sampling and analytical challenges as microplastics, the literature on flow estimation is definitely lacking, and the few articles published rely on completely different methods (see Chapter 1).

2. Quantifying and characterizing microplastics

The various steps introduced to quantify and characterize fibers and microplastics in this work include: sampling, sample purification, observation, and characterization. For urban samples containing high amounts of organic and mineral debris, all these steps are necessary. As presented in the first chapter, any homogeneity among the various published studies regarding methodology is extremely limited. This section is not intended to review the methods employed in the literature but instead will discuss the questions posed in Figure 58; therefore, only some references have been selected to illustrate the issues raised, and they will provide some answers and recommendations for application to further works.



| | |
|----------------------------------|--|
| Sampling | Cut off vs. volume? |
| Sample purification | Which protocol to remove organic and mineral debris? |
| Observation and characterization | FTIR vs. Raman? |

Figure 58: Key methodology-related questions raised during this work.

2.1 Sampling

In this study, the sampling methods used have varied depending on the studied compartment and targeted plastics fraction. The choice of method has raised many questions, but the most important one is related to the compromise between mesh size (sampling cutoff) and sampled volumes. Using a smaller mesh size limits the possibility of sampling high volumes, given that high-volume sampling requires larger mesh sizes. Different particles, as characterized by their size and occurrence, call for different sampling cutoffs and volumes to be collected.

a. Sampling cutoff

Microplastics are unique contaminants characterized by a continuum of sizes from 1 μm to 5 mm and often sampled by nets (Eriksen et al., 2013; Hidalgo-Ruz et al., 2012; Imhof et al., 2012; Moore et al., 2011) or sieves (Carr et al., 2016; Murphy et al., 2016), through which the microplastics, particularly the thin fibers, can pass. Various mesh sizes have been used in river water studies (see Chapter 1), including 800 μm (Moore et al., 2011), 500 μm (Lechner et al., 2014; Moore et al., 2011), 330 μm (Mani et al., 2015; McCormick et al., 2014; Moore et al., 2011; Yonkos et al., 2014) and 112 μm (Zhang et al., 2015). As a consequence, results are not easy to compare.

In this work, the urban compartments have been sampled without any size segregation, i.e. on raw samples. In contrast, the freshwater environment was sampled with two mesh sizes (80 μm vs. 330 μm). A bias is introduced due to the chosen cutoff. Moreover, the real sampling cutoff, even if correlated with mesh size, differs to some extent. While it is impossible to directly estimate the probability of particles passing through a predetermined mesh size, comparisons among mesh sizes and an observation of the particle size distribution can assist future works in selecting the right mesh size.

The average concentration of fibers collected with the 80 μm mesh net equals 44 fibers. m^{-3} , upon examining the results presented in Chapter 5. For five samples not included in this thesis, sampling with a 330 μm sized net yields an average concentration of 0.18 fibers. m^{-3} . This difference indicates that using the 80 μm mesh size rather than the 330 μm increases the probability of sampling fibers by 250 times. This result is marginally lower than what was estimated in a study that found three orders of magnitude more microplastics in the 80- μm net (Norén, 2007).

For the fibers sampled in this work, none with a length shorter than the mesh size were observed. The smallest fiber observed with the 80 μm net was 90 μm , with between 4% and 25% of the fibers being 330 μm or smaller. On the other hand, some fibers display an average diameter of 25 μm , i.e. less than the 80 μm mesh size. It is difficult to determine whether a fiber would pass through a certain sized mesh. Such a determination would depend not only on its size but also on its 3D positioning since passing would be facilitated completely parallel to the meshes and hindered perpendicular to the meshes.

As regards the fragments sampled with 330 μm , for one of the samples taken here as an example, the mean size equals 736 μm (in the longer dimension). The range encompassing these fragment sizes lies between 72 and 2,988 μm , with 24% of the fragments exhibiting a larger dimension less than 330 μm . The reason why these fragments did not pass through the net seems unclear. We could expect that they were agglomerated with or adsorbed to larger natural particles during sampling. Their passing could have also potentially been prevented by larger debris already on the net when the fragments arrived. This debris, mainly vegetal, is potentially capable of reducing the cutoff. Even though the collected fraction is now accessible, still no idea of the fraction passing through the net can be generated. While some small fragments ($< 330 \mu\text{m}$) were sampled, we can suspect that a larger number went uncollected. Moreover, for particles only slightly larger than the mesh size, forcing through the mesh could have occurred due to the force created by the current.

Consequently, typical results regarding microplastic pollution should always be treated with caution. Representativeness depends on the cutoff and has yet to be determined. Further tests could be conducted in order to derive a more precise idea of what is passing through the nets. Sampling with a device that couples various mesh sizes, one directly behind the other, could help address this query. A laboratory test could also be performed with lab-made fibers (Cole, 2016).

b. Sampled volumes

One simple way to avoid the mesh size cutoff issue would be to include bulk samples. The low concentration levels of fibers and microplastics in some matrices however would make it impossible. In general, the ideal volume to be sampled should depend on the contamination levels. Research articles should also always provide information on the sampled volume since this parameter affects the observed contamination levels.

For some urban compartments studied in this work (urban runoff, WWTP effluent, CSOs), only small volumes could be considered because it was impossible to use net sampling and due to technical reasons. It appeared that the fiber levels were high enough to be observed in all compartments. In contrast, fragment contamination levels in WWTP effluent were too low to

be collected in the specified volumes. Similar volumes proved to be sufficient for collecting very high numbers of fragments on CSOs.

Freshwater within the Paris agglomeration showed very dissimilar levels of fibers and fragments and required sampling at different volumes to collect a significant number of each (2 m³ for fibers and 50 m³ for fragments). The volume necessary did not solely depend on the compartment but on the site as well. In Ho Chi Minh City, the fiber levels were so high that bulk samples yielded a very high number of fibers.

The tradeoff between required volume and limited mesh size is one of the most critical issues to resolve during a microplastic sampling campaign. The need for relatively high volumes, to be determined based on the compartment and microplastic shape and size, contrasts with the need to consider plastic debris on a continuous scale without size segregation. With the size distribution revealing that smaller particles are more heavily concentrated than larger ones, a possible solution would be to proceed with various samplings using different mesh sizes (from bulk samples to large meshes like 2 mm) and various volumes, as dictated by the targeted microplastic size. The approach carried out in this work, with the 80 µm and 330 µm nets, has partially addressed this goal. It could be also possible to separate the small microplastics (< 1 mm) from the large microplastics (1 – 5 mm) as previously advised by another work (Imhof et al., 2012).

Table 18: Summary of the cutoff and sampled volumes adopted for each compartment, with consequences on the representativeness of fibers and fragments levels. Keep in mind that with an observation limit lying around 50 μm , the cutoff was considered nonexistent if determined solely by the filters (1.6 μm).

| | Cutoff | Sampled volume | Conclusion for fibers | Conclusion for fragments |
|--------------------------|---------------------|--------------------------|---|--|
| Indoor air | No size segregation | 2 - 5 m^3 (air) | Method adapted to sample fibers | Less than one fragment per 5 m^3 => larger volumes required |
| Atmospheric fallout | No size segregation | Continuous monitoring | All fibers are included | Very low fragment levels |
| Urban runoff | No size segregation | 100 - 1,000 ml | All fibers are included | Fragments in some samples => larger volumes would help increasing the representativeness |
| WWTP samples | No size segregation | 100 - 2,500 ml | All fibers are included | Less than one fragment per 2,500 ml => larger volumes required |
| Combined sewer overflows | No size segregation | 500 - 1,500 ml | All fibers are included | Sufficient volume |
| Seine River | 80 μm | 0.2 - 4 m^3 | The amount of passing fibers must be determined. Samples larger than the 330- μm mesh size net | Volume too small to collect fragments |
| | 330 μm | 50 - 200 m^3 | Passing through the net not sufficiently constrained. The 80- μm mesh size is preferred. | Volume allows for collecting fragments |
| Saigon River and canals | No size segregation | 300 ml | All fibers are included | Volume too small to collect a significant sample of fragments |
| | 300 μm | 0.2 - 148 m^3 | Passing through the net not sufficiently constrained. The 80- μm mesh size is preferred. | Volume allows for collecting fragments |

2.2 Sample purification

As presented in Chapter 2, sample purification is a crucial step in quantifying and characterizing microplastics within urban environments.

For the first step, which consists of organic matter removal, a previously published protocol using SDS, enzymes and H₂O₂ was adapted (Mintenig et al., 2014). According to the literature, organic removal is not systematic. In consulting the complete methodological review published in 2012, this step is entirely absent (Hidalgo-Ruz et al., 2012). The need for such purification has appeared more recently with continental, biota or wastewater effluent samples. Some biota-rich marine samples must also be treated. Studying microplastics in organisms requires digesting the organism body as well. The choice was made in this work to avoid strong acids or bases. Even though several works have used strong acids or bases in the past, like HNO₃ (Van Cauwenberghe and Janssen, 2014), tests have shown that these agents could affect plastic polymers (Claessens et al., 2013; Cole et al., 2014).

A recent article aimed at developing a protocol for extracting and characterizing microplastics in seafood tested the impact of HNO₃ and KOH on 15 different polymers, including all the plastic polymers encountered in the various compartments of this study (Dehaut et al., 2016). HNO₃ led to a significant degradation of PA and in some instances a melting of PS, in addition to a yellowing for all polymers. Use of a 10% KOH solution to extract microplastics appears to be more promising. The solution did not alter the integrity for all polymers tested except cellulose acetate (CA) and was considered the best compromise between extraction and microplastic identification; it provides an effective digestion for mussels, crab and fish tissues. We might expect good digestion as well for urban and freshwater samples. In future investigations, this solution should be tested since it is more time efficient than the one used herein (only 24 h of incubation) and should be less expensive than any enzyme-based protocol.

Moreover, in this work, the SDS and enzyme amounts added were similar for all samples. It might be more pertinent to develop a protocol for greater adaptability to the sample. Measuring the TOC (Total Organic Carbon) prior to treatment would, for example, indicate the organic charge on the sample and help identify the right amount of reactants and enzymes as a result of this organic charge.

The second step consisted of removing the mineral fraction. As presented in Chapter 1, NaCl is often used in the literature at a density between 1.2 and 1.4 g.cm⁻³. In this work, ZnCl₂ with a density of 1.6 g.cm⁻³ has been employed. The NaCl solution is much less expensive than ZnCl₂, and the separation phase is often quicker. Moreover, a cleaner solution can be obtained

with the NaCl since some natural mineral particles (mainly clays) encountered in the Seine and Marne River samples do not settle on the ZnCl₂ solution. Nonetheless, the majority of polymers identified have a low enough density to be buoyant on a solution of NaCl, e.g. PET has a density ranging between 1.37 and 1.45 g.cm⁻³ (Hidalgo-Ruz et al., 2012). The density of the virgin polymer can increase if additives or adsorbed molecules are present in/on the fibers. Consequently, it is suggested to always use a solution with a density close to that of the ZnCl₂ solution. A study tested ZnCl₂ efficiency and found a recovery rate between 95% and 100% for different polymers including PVC (Imhof et al., 2012). Using higher densities is not advisable owing to the fact that the separation would be less efficient.

2.3 Characterization

As presented above, only a small proportion of the particles presented in this thesis were actually subjected to the chemical characterization step. It is important to produce estimations of observation reliability. A study showed that a zero plastic particle count by mistake was dependent on the size of the considered particles (Lenz et al., 2015). These authors determined that for particles smaller than 50 µm, only 63% of the counted particles are confirmed as plastics. On the other hand, 67% of particles between 50 and 100 µm were really plastics. Visual counting is more accurate for particles larger than 100 µm, with 83% of the particles successfully identified as plastics. Like in our work, 50 µm was set as the lower observation limit and the 50 - 100 µm fraction was negligible; it may be assumed that a high proportion of the particles counted would correspond to plastics. While the proportion of particles counted by mistake as microplastics has already been estimated, the amount of overlooked microplastics has yet to be determined. For purposes of this thesis, FTIR microspectroscopy has allowed identifying the polymers of analyzed particles, as opposed to Raman microspectroscopy, which proved to be ineffective.

FTIR microspectroscopy has been used in the vast majority of studies published since the initial one by Thompson in 2004 (Hidalgo-Ruz et al., 2012; Thompson et al., 2004). More recently, Raman microspectroscopy was successfully used in a number of studies (Collard et al., 2015; Dehaut et al., 2016; Imhof et al., 2013; Lenz et al., 2015; Van Cauwenberghe et al., 2013).

Raman microspectroscopy is a promising method that offers an intrinsically smaller spatial resolution than FTIR (because it operates in UV, Near-Infrared and visible regions) as well as the potential for automated mapping. Nonetheless, a persistent high-fluorescence background prevented the identification of colored fibers, which represent the overwhelming majority of our samples.

This method was found to be capable of analyzing particles as small as 1 μm in a study (Imhof et al., 2016). Since mapping of the entire filter was considered time-consuming, the authors decided that large particles would be manually identified while small selected spots on the filter would be mapped for the smaller particles (i.e. 1 - 500 μm). This work excluded some of the colored particles due to the fluorescence preventing their identification. As a solution for the more easily detected particles, the authors proposed proceeding with "bleaching" as a means of reducing fluorescence. The bleaching step consists of illuminating the particle with a laser before starting spectrum accumulation. This paper is one of the few publications to briefly discuss the difficulties related to Raman microspectroscopy. The literature indicates a lack of the knowledge that would help the community overcome some of the complications related to fiber and microplastic identification when using this method.

One study provides a well-rounded and comprehensive synthesis of the use of Raman microspectroscopy for plastic identification: it reported a high success rate using a 455-nm laser beam (Lenz et al., 2015). The authors noted that dyes typically used in the textile industry have minimum fluorescence at the blue excitation wavelengths (458 nm – 488 nm). Our fiber identification tests benefited from access to the 638 and 785 nm laser beams, which were completely masked by the fluorescence signal orders of magnitude greater than Raman scattering. Further investigations are needed to reveal optimal instrumentation and excitation wavelengths for the application of Raman spectroscopy to fiber and microplastic analyses.

FTIR microspectroscopy has been applied more systematically and straightforwardly in our case. It has required selecting fragments visually, which is a time-consuming process. Most studies using FTIR have employed this same approach (Browne et al., 2010; Ng and Obbard, 2006; Thompson et al., 2004). Modern equipment developed for FTIR can help overcome this constraint by means of mapping. A study has demonstrated the possibility of efficiently using an FTIR mapping analysis based on detection tracking a combination of polymer-specific

regions of absorbance (Harrison et al., 2012); it was observed that the mapping of 3-mm² areas detected 69% of the PE fragments present. A more recent study reported a 98% successful identification rate using mapping with a focal plane array (FPA)-based FTIR microspectroscopy method (Tagg et al., 2015). FPA detectors allow for the simultaneous acquisition of a high number of spatially resolved spectra. Each pixel provides an independent infrared spectrum, making it possible to acquire thousands of spectra within minutes. The complete mapping on a single filter of the same size as those used herein (i.e. diameter: 47 mm) could be completed in less than 9 h using this method.

A very recent study compared FTIR and Raman mapping (Käppler et al., 2016), showing that FTIR found up to 35% fewer microplastics than the Raman method, especially for particles smaller than 20 µm. Their study suggests that FTIR should be used for rapid and reliable analyses with particles larger than 50 µm, while smaller particles should be analyzed with Raman spectroscopy, which is more time-consuming. Until now, mapping efforts have been very minimal yet of utmost importance especially for samples in urban areas, where particles are very high in number and require automated, less time-consuming methods. It has to be kept in mind that the efficiencies discussed here are dependent on the used instruments and shouldn't be generalized.

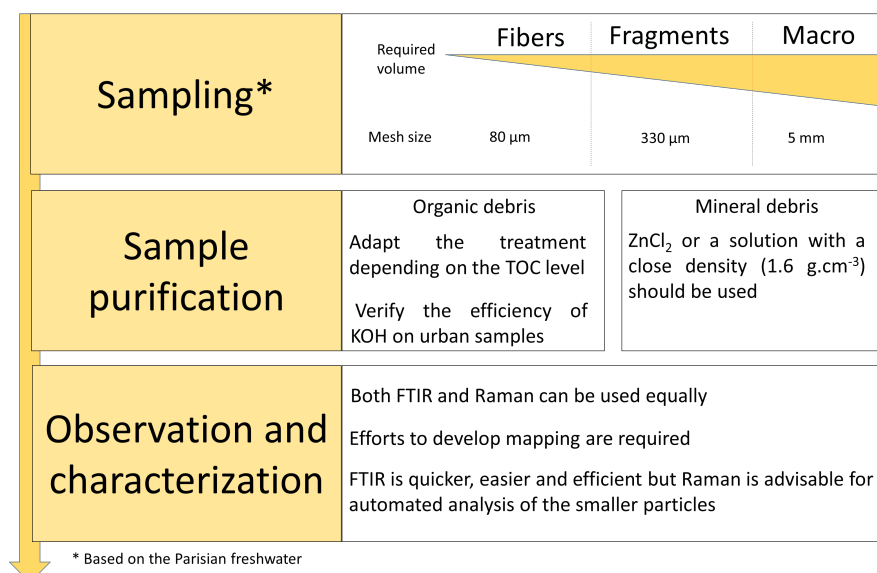


Figure 59: Recommendations and perspectives regarding microplastic analysis.

3. *Microplastic definition in relation with the nature of the polymers*

In this work, all textile fibers have been counted and taken into consideration. Only afterwards did characterization help estimate the synthetic fraction. In other works, non-synthetic fibers are automatically dismissed and only synthetic ones, considered to be microplastics, are included in the results (Browne et al., 2010; Hidalgo-Ruz et al., 2012; Thompson et al., 2004). This protocol has been based on the fact that studies often restrict the definition of plastics to polymers stemming from petrochemicals. This term "microplastics" as found in the literature remains rather ambiguous and encompasses a broad spectra of polymers and shapes. Its use differs among the various articles in the literature, although a microplastic is most commonly defined as any particle smaller than 5 mm and derived from petrochemicals. Rayon was once included in the microplastic count (Lusher et al., 2013). In contrast, cellulose acetate has also already been considered as a microplastic despite not being derived from petrochemicals (Dehaut et al., 2016).

While the microplastic definition based on particle size and shape characteristics is often discussed, no attention however gets paid to the nature and chemical definition that should be ascribed to a microplastic. As pointed out in Chapter 1, the definition of plastic is not inherently simple, a feature that affects the microplastic definition.

Given that the microplastic topic is mainly environmental, the definition of a microplastic should be based to a great extent on its potential impact. The fact that both natural and artificial fibers (principally rayon) have been neglected due to the commonly held perception that their rapid degradation does not cause any environmental damage. In our work however, rayon fibers were found in freshwater. Rayon had also already been found in previous works in marine environments and even in the gastrointestinal tract of fish in the English Channel (Lusher et al., 2013, 2014). The presence of rayon in these fish indicates that, even though rayon is more readily degradable than synthetic fibers, it can still bypass wastewater treatment, be transported into the environment (by air, given that rayon was observed in atmospheric fallout, or by water), and stay long enough until being ingested.

One type of rayon, viscose, was also found in the gut of various macrofauna species living in the Mediterranean. These species were of various trophic levels. The same study identified

two dyes on the rayon fibers, i.e.: direct red 28, and direct blue 22 (Remy et al., 2015). The authors also pointed out that these dyes are known to be carcinogenic for vertebrates.

Other authors have indicated that cotton-based fibers can not only adsorb pollutants and contain many additives, but they can also facilitate pollutant and fiber availability to organisms through being degraded; on the other hand, synthetic fibers would deny the pollutants availability to the surrounding environment (Ladewig et al., 2015).

As research has become focused on synthetic fibers, greater efforts are now needed to compare the natural and artificial categories. Degradation rates, as well as capacities to interact with both the pollutants and the biota, must be determined in order to better estimate the potential impact of these fibers.

4. *Microplastics: a generic word for many sizes, shapes and polymers*

Plastics found in the environment can have very different sizes, from large macroplastic debris to tiny textile fibers. They also display a very broad spectrum of shapes, including plastic fragments, microbeads, pellets and fibers. Moreover, even when considering just petrochemicals, a long list of polymers can be encountered. Man-made, non-petrochemical particles can also be found, like rayon fibers or rubber fragments. Consequently, all these particles must be assessed in the environment and categorized accordingly to generate a comprehensive overview.

These various particle types may be included under the generic term "microplastics" even though they have all undergone different mechanisms and dynamics. These diverse particle types also stem from varying sources. In this work for instance, it was shown that WWTP effluent is mainly a source of fibers, while fragments are present in rainwater and highly concentrated in CSOs. Fragments might also be mainly produced in the environment from a degradation of macroplastics, which is generally not the case for textile fibers and other primary microplastics. The fate and potential impact of different polymers and particle types may also differ.

We advise that results from distinct types of microplastics should always be discussed separately, depending in large part on the aim of the study. For instance, all textile fibers should be considered together in opposition to fragments when it comes to the identification of the sources. On the other hand, a categorization by polymer type is necessary when dealing with degradation processes. Other examples on how particles can be categorized depending on the goal of the investigations are illustrated on the figure 4. The global environmental impact of a particle is determined by a combination of the listed characteristics (which is not an exhaustive list). As a consequence, each particle type would have a different global impact.

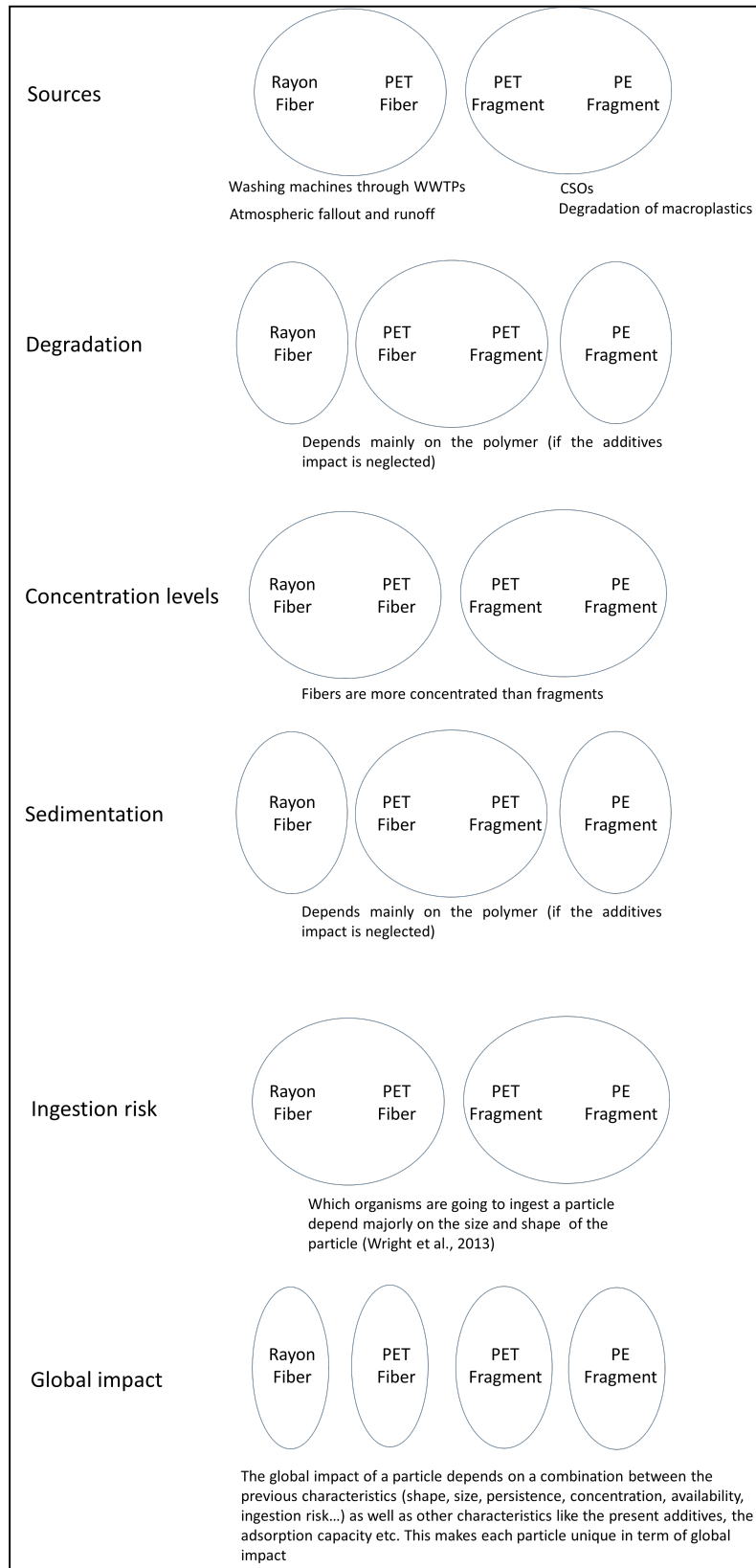


Figure 60: particle types used to illustrate the potential differences in microplastics depending on their shape and polymer.

III. Perspectives to this study

When this work program started up in 2013 and until now, a large number of studies focusing on microplastics have been carried out (Chapter 1). In taking into account this body of literature and the advances and findings that the present thesis has enabled, a list has been drawn up of the main challenges that need to be overcome in the near future, as well as the perspectives emanating from this work.

- **Macroplastics in the Seine River**

The amount of macroplastics flowing in the Seine River within the Paris agglomeration was successfully determined during this study program. Further work is required however to identify the amount actually reaching the estuary and entering the English Channel. Transport time also needs to be determined. To provide answers, we could associate plastic debris with GPS trackers in order to assess the fate and transport time of the debris. Moreover, the collection efficiency of booms could be estimated according to the same method.

During its transport, some plastic debris will deposit onto the banks of the Seine and be collected during cleanup operations. Accumulation zones on the banks between Paris and the estuary should be demarcated, with a determination of the amount of plastics trapped in these zones. The quantity of deposited plastics remobilized during flood events is also unknown and degradation processes for deposited macroplastics must be identified as well.

Moreover, the inputs of plastics between the Paris agglomeration and the Seine River estuary need to be estimated.

- **Microplastics analysis methods**

During this thesis, the investigation of microplastics in urban compartments was very time-consuming. Consequently, the statistical findings of this work were limited for some compartments, mainly due to the possibility of considering just a small amount of samples. It is of utmost importance to develop more time-efficient methods to help future projects gather more extensive information. The most time-consuming step involved the full count of fibers collected on the heavily concentrated urban samples. As proposed earlier, a simple mapping of the filters using a spectroscopic method, either FTIR or Raman, would be very useful.

- **Indoor air**

For the first time, this work estimated and characterized textile fibers, including microplastics, in indoor air. Very little is known about the potential impact of these fibers. While the detection limit applied herein was reduced to the 50- μm scale, further work should be carried out on even smaller fibers. The potential of inhaling these fibers must also be determined and all potential impacts urgently identified.

- **Atmospheric fallout**

Atmospheric fallout has proven to be a source of both artificial and synthetic fibers in an urban context. Urban runoff analyses have shown that a proportion of these fibers will deposit on urban surfaces and then be released into freshwater. This study presented a long monitoring on two sites. The representativeness needs however to be identified.

The atmospheric compartment needs to be further investigated as regards the potential input represented for the marine environment. While rivers have often been viewed as the main pathway of continental microplastics into oceans, the atmospheric compartment might, via its long-range transport, also be a significant contributor. Installing atmospheric fallout collectors at sea would help address this issue.

- **Urban water**

This work has assessed the amount of fibers and microplastics at different stages of their transport from greywater to the WWTP outlet; it has highlighted the ubiquity of fibers while fragments were mainly identified in CSOs. The dynamics of these particles during their transport in the sewer system should be better identified in order to understand the observed levels and fiber-fragment distribution pattern.

This study has estimated fiber removal through two WWTPs and for two stages (i.e. primary and secondary treatment). A more precise determination is still required for the fate of the removed fibers. We would not expect these fibers to degrade during the treatment, but they could be removed during screening or trapped in the sludge or grease.

An overview of fibers and plastics in an urban system has been provided in this thesis. To complete an assessment of pathways in the continental environment, agrosystems would

need to be considered. Soils might actually be contaminated from atmospheric fallout as well as from sewage sludge amendment (Habib et al., 1998; Zubris and Richards, 2005). The impact on soil fauna must be identified, along with the fate of particles and their runoff.

- **Freshwater sampling**

For its freshwater analysis, this study has reused the classical net sampling method typically employed in the literature, yet with two distinct mesh sizes. To better assess the pertinence of such sampling methods, it is necessary to identify the best balance between the cutoff and sampled volume. A comprehensive overview of the microplastic size continuum requires a more systematic coupling of small-sized nets with the more widespread 330 μm net.

This study highlighted also issues related to the representativeness of the samplings in rivers. Because of the time consuming aspect of microplastic analyses, the number of samplings during long monitorings have to be limited. This work provides preliminary knowledge on the short spatio-temporal variability. Nonetheless, a better indication on the representativeness is still required. The role that uncertainties related to sampling and analyses play on the observed patterns, estimated fluxes and drawn conclusions is yet to be accurately identified.

- **Fibers in freshwater**

The present study has helped fill some major knowledge gaps regarding the inputs, presence, occurrences and spatial distribution of fibers in the river. Yet on the other hand, fiber dynamics remain poorly understood. Future investigations should focus on answering the main questions this work has raised, with the most important one pertaining to the role of the potential various sinks.

A recently launched project, financed by ANR (France's National Research Agency), is aimed at investigating various pathways for the transport and fate of microplastics in the marine environment; among other things, it studies the processes of fragmentation, colonization, additive leachate and organic pollutant sorption, ingestion, sedimentation and re-suspension (<http://imm.univ-lemans.fr/fr/thematiques/polymeres/projets-polymeres/nanoplastics.html>). A similar approach should be initiated for the freshwater system.

The most urgent process to evaluate would be sedimentation since it could significantly affect microplastic fluxes. To better understand the patterns observed, more samples should be extracted both upstream and downstream of the analyzed points. It is in fact possible that all sites monitored in our study are being subjected to similar anthropic pressures, thus explaining their similar levels. Heading downstream could result in finding smaller concentrations. The re-suspension and dynamics in the benthic boundary layer also need to be further explored.

- **Fragments in freshwater**

Fragments should be investigated to the same extent as proposed above for fibers. In addition, fragments prove to be a major source that needs to be evaluated. Macroplastics in the Seine River will potentially produce a number of secondary microplastic fragments. While non-systematic and other diffusive sources of microplastics are starting to be understood, the rate of appearance of secondary microplastics remains completely undetermined. One perspective from this work would be to correlate the amount of plastics present in the Seine River (determined in Chapter 3) with the degradation rate of plastic material under freshwater conditions. While the amount of fragments in the Seine around the Paris agglomeration could be determined in this thesis, we would expect for instance an increase in fragments towards the estuary due to the production of secondary microplastics from degradation.

Let's keep in mind that the observed fiber/fragment ratio might be very characteristic of the sites studied herein. For a better idea of actual inputs into the marine environment in terms of particle types and flux levels, estuary-based analyses are mandatory.

- **Regional context**

It was showed that levels of macro and microplastics are far higher in the Saigon River and its canals than in the Seine River. Record levels of microplastics were also observed in urban rivers and water in China (Wang et al., 2016). Regional characteristics, as the waste management policies and infrastructures or the waste water treatment impact highly the plastic inputs and contamination. Results should always be interpreted with caution and with the perspective of local conditions. Studies must be carried out in different locations worldwide in order to be able to have an accurate idea of the plastics fluxes.

- **Impact of microplastics**

The ecotoxicological risk of microplastics was only briefly discussed herein since this issue lies beyond the present scope. It is important however to recall that one of the purposes of determining microplastic concentrations in freshwater is to help subsequent works investigate the potential impact of this contamination category. The ecotoxicological risks of the various particles and polymers found in the Seine River should be assessed with respect to freshwater species. It would be beneficial to expose the species to water with a similar microplastic composition in terms of shape, size and polymer type to that presented herein. It should also be asked whether artificial fibers could represent an environmental risk. If confirmed, they would need to be more systematically included when quantifying microplastics in the environment.

- **A modeling approach**

A modeling approach would help answer the main questions raised regarding microplastics in freshwater. The coupling of a mechanistic model of the physical subsystem with the various mechanisms that the different particles can experience will be necessary in a near future. These mechanisms could include sedimentation, re-suspension, fragmentation and riverbank deposition. Constants dependent on the particle polymer, its density, shape and size could be introduced into these models. In this manner, the behavior of particles in freshwater as well as their fate could be determined.

- **Operational implications**

This thesis has adopted a global approach to estimating fiber and microplastic fragment levels in various urban system compartments. It has contributed new knowledge on the sources of these contaminants and their characteristics in urban environments. These data could be beneficial when implementing the marine strategy framework directive (MSFD) (Galgani *et al.*, 2013), which aims to achieve a good environmental status for European marine waters by 2020. An MSFD "10" indicator relative to marine litter explicitly indicates that for marine plastic and microplastic pollution, the solution entails tackling the problem at its source. This work has helped understand the nature of this source; for the first time, it has shown that atmospheric fallout must be considered to properly estimate all sources. It has also revealed that a megacity such as Paris is, in terms of microplastics, mainly emitting fibers into the

environment. WWTPs are a major source of input for these fibers. In contrast, the major masses of plastics flowing on rivers contain macroplastics. To protect marine waters from plastic pollution, in accordance with MSFD, these macroplastics should be addressed as a priority.

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Abstract

Plastic pollution in the marine environment has been widely studied since 1972, with most research being performed after 2004. Investigations into plastic pollution in freshwater and especially in urban catchments only got underway at the beginning of this decade; urban plastic pollution sources and their related fluxes in rivers remain largely unknown. Special attention should thus be paid to the level of plastic contamination in catchments exposed to severe anthropogenic pressures, notably in urban areas. This Ph.D. thesis focuses on the case study of the Paris agglomeration and its impact on the Seine River. A dual approach has been carried out with both macro- (> 5 mm) and micro- (< 5 mm) plastics taken into consideration.

The quantity of macroplastics conveyed by the Seine River was estimated by a field study and through application of a theoretical approach.

Regarding microplastics, fibers (made with synthetic as well as man-made polymers) and fragments were both evaluated in different compartments of the urban system. This study has targeted: the air compartment (indoor and outdoor air, plus atmospheric fallout), the sewer system (from washing machine disposal to WWTP influent and effluent), and the inputs during wet weathers periods, i.e. runoff and combined sewer overflows. Fiber and fragment contents were also determined in the Seine River.

This work is intended to provide relevant methodological insights into the sampling of microplastics in rivers. Two mesh size nets were tested (80 μm vs. 300 μm). The homogeneity of fiber distribution in rivers has also been verified by assessing short-term temporal and spatial variabilities. To highlight the potential impact of the Paris agglomeration, a monthly monitoring campaign at 5 sites upstream and downstream of Paris was conducted as well.

This thesis has mainly highlighted the ubiquity of fibers in all compartments. Fibers were found to be predominant in comparison with fragments across all compartments. Combined sewer overflows exhibit rather high amounts of fragments. On the other hand, the flux of microplastics in the Seine River was shown to be negligible in terms of mass relative to that of macroplastics. This study is also the first to demonstrate that the atmospheric compartment must be considered as a significant potential source of microplastics.