CHAPTER

3

Sampling and analyzing microplastics in rivers: What methods are being used after a decade of research?

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3.1 Introduction: A fast-evolving research area

While the presence of plastic particles in marine environments was evidenced in 1972 with two publications (Carpenter et al., 1972; Carpenter and Smith, 1972), it was only after the now-famous paper "Lost at sea: where is all the plastic "that the scientific community took an interest in microplastics (Thompson et al., 2004). The attention on these particles smaller than 5 mm has since exponentially grown within the academic sphere while attracting attention from media, general public, and policymakers.

Microplastics have now been shown to be ubiquitous in the environment and were even found in remote areas (Dong et al., 2021; Frank et al., 2021a; Yang et al., 2021). This pollution was first described as a marine pollution (Cole et al., 2011), and the presence of these particles in estuaries was first evidenced in a 2010 study (Browne et al., 2010) along the shorelines of the Tamar Estuary (UK). The scientific community quickly pointed at rivers as a possible major source of microplastics. It was stated as early as 2009 that 80% of the plastic pollution detected in marine environments stems from a terrestrial source (UNEP, 2009). This widely cited

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estimation has been poorly substantiated but allowed attention to be drawn into rivers, a potential major pathway for marine microplastics. The earliest study we found dealing with this topic is from 2011 and identified the presence of microplastics in two urban rivers of southern California (Moore et al., 2011a, b). In this work, the authors used hand nets for sampling but also manta trawls, which is a practice transposed from marine environment studies. Debris was then sorted out under a dissecting microscope, and samples did not undergo any treatment. Many other studies were carried out on microplastics in river waters with evolving methodologies in the past decade, and many reviews addressed this topic (Akdogan and Guven, 2019; Koelmans et al., 2019; Mendoza and Balcer, 2020).

In a first book chapter we published in 2018, we referenced 22 existing studies on microplastics in rivers (Dris et al., 2018b). Only 3 years later, 76 studies were found for 2021 alone. The previous chapter showed that differences between studies in the methods used hamper the comparability of the data. This lack of homogeneity makes it complex to draw conclusions or general patterns. The review also stated that *"it is still a long way until routine monitoring approaches are established."*

Researchers dealing with this topic seem to agree with this perception, and most reviews on microplastics (all aspects and matrixes included) mention a lack of comparability between studies (Beaurepaire et al., 2021; Dris et al., 2015; Koelmans et al., 2019). The first review on methods to analyze microplastics by Hidalgo-Ruz and coauthors already pointed out in 2012 an urgent need for methodological standardization (Hidalgo-Ruz et al., 2012). Nearly a decade of research later, Koelmans and coauthors wrote in another review: "*We conclude that based on the limited number of high quality studies identified, standardization of microplastic analysis in water is needed*" (Koelmans et al., 2019).

This demonstrates that while academics identify and agree upon the need for homogeneous methods, it remains challenging to achieve. Various methods were established simultaneously as numerous parallel studies and methodological developments were carried out by researchers worldwide. An early establishment of standardized and homogeneous methods would have been counterproductive as it would have significantly limited any methodological progress. Differences are also necessary sometimes due to differences in the scientific objective of studies. With the multiplication of studies and publications on the topic, it becomes increasingly hard to draw a pattern on the methods used and have a global assessment on the present state of knowledge on the approaches used to assess the occurrence and types of microplastics. By doing a keyword search in Scopus with *"microplastic,"* a total of 5347 publications were found, with only seven in the year 2011 and 2043 published in 2021 (on the 31st December 2021, which represents also the cutoff date for the corpus of the present study).

This chapter aims at providing an overview of the studies carried out on microplastics in rivers. It focuses mainly on the methods used in all the studies to assess better the current state regarding the heterogeneity of the used methods on the one hand and their reliability on the other. It first provides an objective and factual view on the current practices and tendencies for assessing microplastics in freshwater. It will help provide an up-to-date understanding of how academics approach microplastic pollution research. These tendencies are later discussed and evaluated to draw concrete conclusions and provide recommendations and guidelines for future studies.

3.2 Approach used to build and analyze the corpus

In order to build the corpus used in this chapter, we used the following query in the Scopus bibliographic database: Microplastic AND River, in the "Article title, Abstract, Keywords" field. In order to work with a fixed corpus, and as most of this work was written during 2022, all papers more recent than 2021 were excluded. Papers not in English and reviews were also automatically excluded via Scopus. This approach provided a list of 705 papers. In this list, the authors worked together on removing manually all the papers out of the scope of this study: only papers analyzing microplastics in rivers (water and/or sediments) were kept. For instance, ecotoxicology or modeling studies were removed from the corpus. Studies focusing on the biotic compartment were also excluded. After a thorough double-checking, 175 papers remain in the corpus. Two journals (*Science of the Total Environment* and *Environmental Pollution*) together comprise more than 35% of the papers in the corpus.

We then made a list of relevant information we want to retrieve from the various studies and identified a list of keywords: 1 mm, 5 mm, acid, ATR, blank, bottle, bucket, bulk, contamination, control, definition, density solutions, enzyme, FTIR, grab, H_2O_2, KOH, mapping, microscope, net, Nile red, pump, PyrGCMS, Raman, recovery, spiking, standardization, stereomicroscope, transmission, trawl, units, visual. With TXM (Heiden et al., 2010), we accurately identified the mention of these topics in the articles. TXM is a free tool dedicated to the exploration of textual corpora for quantitative and qualitative analysis. TXM allows both statistical processing and the identification of the contexts of occurrence of the results of finely tuned queries. These queries, built according to the CQL (Corpus Query Language) rules, draw on the morpho-syntactic labeling carried out by the tool when texts are imported. They are similar to regular expressions (regex). Each keyword is therefore "translated" into one or more queries in order to identify the different orthographic or conceptual variants (i.e., the query [word = ".*FT.?IR.*"%c] retrieves contexts with FTIR, FT-IR, micro-FTIR, µ-FTIR, µFT-IR, m-FTIR, µ-ATR-FTIR…). The contexts (i.e., the 20 words before and after each occurrence) were then analyzed by the authors. These queries are limited to the main body of the text and do not retrieve occurrences from the references cited in the bibliography.

3.3 What parts of the world are covered by studies on microplastics in rivers?

In the studied corpus, we identified 175 studies dealing with the levels of contamination of microplastics in rivers. Among them, some studies focus solely on the water column (84 studies) or the sediments (45 studies), while others tackle both (46 studies). As a consequence, water is analyzed slightly more often than sediments (130 vs 91). This can be explained by the fact that the sediment matrix is more complex and requires more efforts for sample preparation.

We made an attempt to retrieve from all studies the location of all the sampling points, to have an idea of the geographical repartition of the available data. This exercise made it clear that such information is not always easily available. We encountered 61/175 that do not indicate the exact location of their sampling points. The corresponding authors of all these

papers have been contacted (up to five reminders over the course of 1 year when no response) and 41 replied and sent coordinates of their sampling points. By combining this information with the data already present in papers, the sampling points of 155 papers have been collected. Most often coordinates are in degrees, but sometimes UTM system is used or Ordnance Survey National Grid reference system in Great Britain. It is important for future studies to include coordinate (in the manuscript directly or in the supplementary material) and that the decimal degree system should be preferred. This will be helpful for a better information exchange with the scientific community. The geographical location is a major requirement for any environmental data.

While the number of sampling stations in each study varies greatly, the median number of sampling points is around 10, regardless of the matrix (see Fig. 3.1). In order to improve spatial representativity when sampling for microplastics, several sampling points are often required. For rivers, an upstream-downstream approach is often relevant to understand inputs and fate of this pollution. While the more points are sampled, the more precise and useful are the results, the time-consuming constraint of analyzing microplastics limits the number of points.

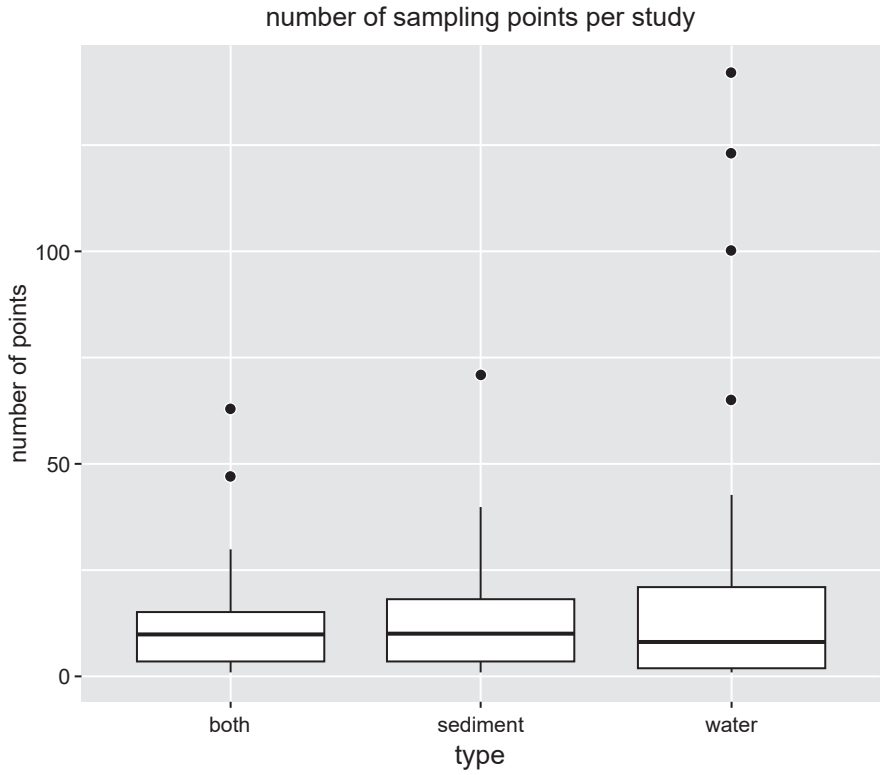

FIG. 3.1 Boxplot of the number of sample points per study, when water, sediment, or both matrices are sampled.

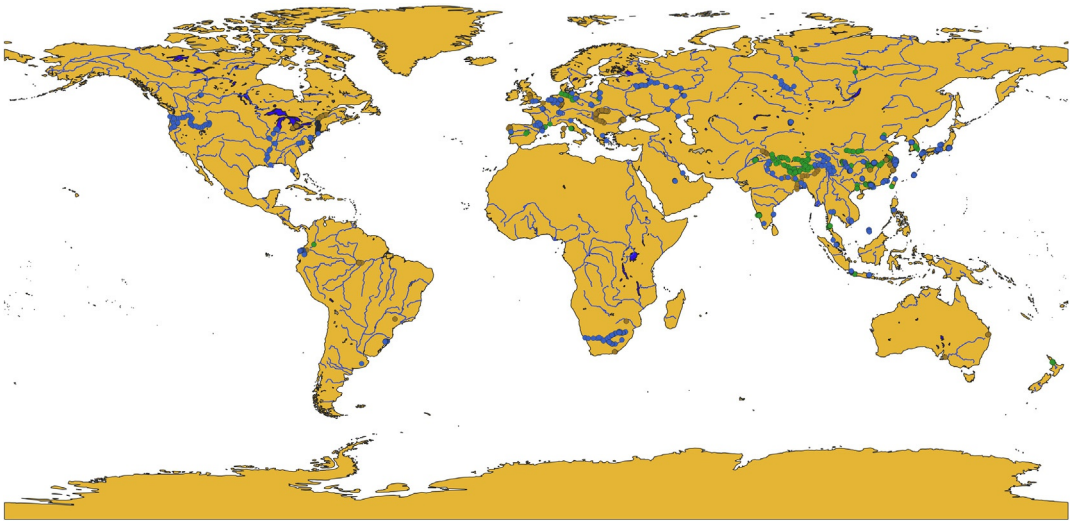

FIG. 3.2 Location of sampling points (*blue*: water, *brown*: sediment, *green*: water and sediment).

Most of sampling occurred in the Northern hemisphere (2040 samples over 2273), in three main regions: Europe (483 points, 40 studies), Asia (1247 points, 73 studies), and North America (417 points, 15 studies). Locations of samples are summarized in Fig. 3.2.

3.4 What size definition is used for the assessed microplastics?

Although there is a continuous distribution of plastic particles from the large-scale debris to sub-micrometric particles, different methodologies can only quantify certain debris size ranges. As a result, in order to facilitate scientific communication and ensure comparability between studies, it is necessary for each study to explicit clearly the definition of the terms used. In particular, the term "microplastic" is a gathering keyword of the community and needs to be precisely defined. In the corpus reviewed in this chapter, two different notions emerge: the theoretical size range of what is considered a microplastic by the community, and the de facto size range that is targeted by different studies, based on the method employed.

The term "microplastic" was first used to discuss small plastic debris in 2004 (Thompson et al., 2004), without any strict size definition. The study highlighted that while large plastic particles had been observed across the environment, microscopic plastic particles were also widespread. A size range of 20–2000 µm was sampled. While the term remained, its definition and use evolved over time. In particular, the first common definition for what constitutes a microplastic particle dates back to 2009 (Arthur et al., 2009): an upper limit of 5 mm was suggested. In this corpus, this upper size limit is close to a consensus: 82.9% of all analyzed studies (145/175) directly or implicitly defined microplastics as plastic particles smaller than 5 mm. Of the remaining articles, six defined or focused on microplastics as particles smaller

than 1 mm (Donoso and Rios-Touma, 2020; Eo et al., 2019; Frank et al., 2021b; Johnson et al., 2020; Rowley et al., 2020; Tibbetts et al., 2018). The remaining articles either did not provide a clear definition of microplastics or provided another, uncommon, upper definition for their study.

While an upper size limit of what constitutes a microplastic is now largely agreed on, wide differences remain between articles regarding the lower size limit of that definition. To begin with, while most documents provide an upper limit for particles to be called microplastics, fewer define a lower limit. In the corpus of articles provided, all articles that provided a lower limit for microplastics provided a limit of 1 μm. Under that limit, particles are defined as nanoplastics. However, current methodologies cannot identify environmental plastic particles around such small sizes. As a result, the lower size limit used by studies in this corpus was not related to the common definition of microplastics, but rather to the targeted size range, related to methodological limits.

The de facto targeted microplastic size range is harder to assess for microplastic studies. It can be determined by the sampling method and its cutoff, the treatment processes, or the lower size detection limit of the analytical methods. In the latter case, while analytical cutoff points represent a hard boundary, particles nearing that boundary are also increasingly less detected. These elements are discussed later in their respective sections.

While the definition of what constitutes a microplastic can reach a consensus, quantification procedures still evolve. As new analytical methods get popularized, smaller size ranges become available for identification. It is likely that in a foreseeable future, the lower limits available for microplastic identification both will keep changing and will not yet come to a common value. As a result, it will remain necessary to clearly mention the precise limits of microplastics studied in each article.

3.5 What methods are used to sample microplastics in river waters?

Among the reviewed papers, 128 sampled water and specified what method was used for sampling. The other two did not provide any information and are excluded from this section. The method mostly used is the direct deployment of a net in the river (64/128). Bulk sampling is carried out in 56 studies, with half of them taking the full sample without any size segregation (28/128) and the other half proceeding to a manual on-site size separation (28/128). The latter is carried out either via a net or sieves. Pumping followed by an onsite filtration is used in the remaining studies (14/128). The sum exceeds 128 because some used more than one method and are therefore counted twice (this holds true for other sections in this chapter and will not be mentioned again).

Plankton nets with a mesh size of 330 μm were originally used to sample the neuston and were transposed for microplastic sampling since the first study (Carpenter and Smith, 1972). This sampling method is still prevalent in marine environments. While a methodological transfer occurred initially, and even if the methodology was often questioned, most studies kept this trend for a comparability purpose. In freshwater, microplastics were sampled for the first time in 2011 in a study by Moore et al. (2011b). While in marine environments and lakes, the trawls are towed using boats generally, here, the net is installed at a fixed point in the river

and the river water flows through the net for a determined amount of time. In rivers, both methods are used as trawls can be towed by a boat (Liu et al., 2020; Park et al., 2020a) or used in a stationary manner (Dris et al., 2018a). Most used nets are plankton nets, manta nets, or drift nets (Donoso and Rios-Touma, 2020).

Bulk samples are a common method for microplastic sampling, usually taken with a bucket, bottle, or another vessel. Bulk samples with size segregation are often chosen as an easy and practical method in comparison to nets. It can be employed even in small streams where nets cannot be deployed. For instance, samples are sampled manually and then poured through portable nets (Eo et al., 2019). Pumping water through a pipe is an efficient method to take large volumes but also target easily the sampling location. Its main advantage is the possibility to sample at various depths, while nets often allow only superficial surface samples.

It became quickly obvious that analyzing microplastics requires often to sample large volumes. In addition to a representativity issue, the rarity of microplastic particles in the water in most locations leads to the necessity to sample certain volumes in order to retrieve enough particles for a correct quantification. As a consequence, an onsite volume reduction is required, leading to a necessary size segregation. The higher the cutoff size, the higher the volume taken (less clogging), but the more particles are lost (smaller ones). Water microplastic studies require to always consider the balance between the volume (representability) and size separation.

Among the 64 studies carrying out net sampling, only 30 revealed directly the sampled volume. More than half of the studies (34/64) did not disclose any information on the sampled volumes, although sometimes the size of the opening of the net or the sampling duration is provided. This information is not sufficient as it does not seem clear if studies take into account the water flow of the rivers. It is advised for all future studies to specify the sampled volume, as it directly impacts the representativity of the results. In the 30 studies sampling rivers with a net and disclosing the volume, the median volume of each study was retrieved. A very wide range of volumes is sampled, from 14.4 to 386,000 L. By taking into account all the studies, the sampled median is of 6500 L. In the bulk sampling followed by an onsite size separation, the sampled volume information is provided much more regularly (26/28). As the sampling and size separation are manual, the sampled volume is much more limited as it goes from 1 to 200 L with a median of 27.5 L. In studies where bulk samples did not undergo any onsite separation, volume information is provided similarly (26 out of 28 studies). As the transport of large volume becomes quickly a limiting factor, between 0.25 and 20 L were sampled in these studies, with a median of 2.5 L. All studies proceeding to pump sampling indicated the sampled volumes, which are between 20 and 10,000 L with a median of 70 L. Net sampling seems to be used more often for larger volumes and potentially a better sample representativity, but this factor alone cannot be considered and the cutoff and sample localization in the column need to be taken into account.

Bulk sampling without any size separation allows to sample very limited volumes, but is the only method that can sample very small microplastics. Oppositely to the volume, all studies indicated the size cutoff of their sampling method. For net sampling, this cutoff goes from 20 to 500 µm with a median of 300 µm. A mesh of around 330 µm (between 300 and 363 µm) is mostly used, in 34 of the 64 studies. Manual size separation of bulk samples used in general a lower size cutoff, from 10 to 300 µm with a median of 50 µm. Pumping was employed to sample smaller microplastics from 1.2 to 330 µm with a median of 39 µm. While pumping allowed

to retrieve larger volumes than manual size separation, it also made studies able to collect smaller microplastics in most cases. As the filtration often happens under a pumping pression, clogging occurs later than in manual size separation, thus allowing a higher volume sampling.

Fig. 3.3 shows all studies in water (100%) along with their sampling size cutoff. When no size separation is conducted, the cutoff was marked as 0. When a study combines two methods, only their smaller size cutoff was retained for this figure. It shows, including all methods, what is the "lost" fraction due to the sampling cutoff. In 50% of the studies, the fraction smaller than 75 µm is lost, while 20% of the studies collect all microplastics. With this exhaustive view, it is observed that 30% of the studies lost the fraction that is smaller than 300 µm. Knowing the risk that smaller microplastics represent, further efforts to quantify this fraction are required. By splitting the studies into two groups, studies before 2021 (73) and studies in 2021 (55), it is observed that the median of the cutoff decreased with time (48 µm in 2021 vs 100 µm before). This median is mainly the consequence of the increase of studies proceeding to a bulk sampling without any size separation (30% of the studies in 2021 vs only 15% of the studies earlier). Net sampling, on the other hand, represented 63% before 2021 while representing only 29% of the studies in 2021. Studies are taking into account the limitations of this methodology, related to the size cutoff, the sampling representativity, but also the reliability of the method. The knowledge on the efficiency of net rinsing in order to retrieve microplastics is limited. Moreover, air contamination is higher using this method in comparison to pump sampling, often carried out with closed systems. The proportion of the use of pump sampling did show a clear evolution trend.

It is crucial to consider that sampling is only one parameter of the size cutoff of the detected microplastics. These data need to be considered with the size limit of the analysis method. This is discussed later in this chapter. Moreover, the cutoff of the net or the filtration is not an exact reflection of the real cutoff. Smaller microplastics can get trapped by a net with a larger mesh, and larger microplastics can still squeeze through a sieve.

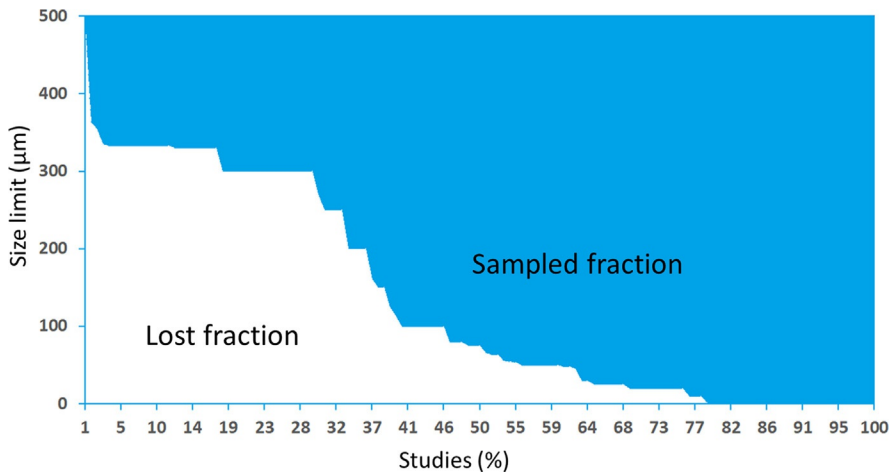

FIG. 3.3 Sampling size cutoff in all studies of the corpus.

3.6 What are the common practices for sample purification?

Investigation on the occurrence and fate of microplastics in the environment often faces difficulties from sample matrix during analysis. The protocol for analyzing microplastics relies on the capacity to separate the plastic particles from the matrix that is rich with particles that impede the performance of the identification step. This matrix is composed mainly of natural particles in the form of organic materials and mineral debris. The separation is based on the different characteristics of plastics from natural particles: their relative resistance to some chemical treatments that can dissolve organic matter, and their low density in comparison to most mineral particles. Until now, several treatment protocols have been developed. The selected preparation protocol needs to ensure certain criteria such as time–cost efficiency, preservation of particles, and separation/removal efficiency.

Different levels of sample purification for freshwater and sediment have been observed in the corpus of reviewed studies. Only few studies applied no specific treatment in their experiments, about 10% and 4% for freshwater and sediment samples, respectively (14/130 for water; 4/91 for sediment). The other studies conducted some sort of treatment (organic material, mineral material, or both) and are reviewed below.

3.6.1 Organic natural material removal

More than 80% of the reviewed papers (107/130) focusing on water samples included OM treatment in their experiments. Hydrogen peroxide (H_2O_2) was the most commonly used chemical in this step. About 53% of studies (57/107) applied H_2O_2 alone with various modifications, e.g., solution concentration (15%–40%), temperature (20–100°C), exposure time (few hours to 7 days), etc. Fenton reaction, in which OH· radicals are continuously reproduced for oxidation process in the presence of Fe^{2+} catalyst, was the most second popular method (37/107). Fenton was first used for river water samples in two publications released in 2014 (McCormick et al., 2014; Yonkos et al., 2014) with the protocol slightly modified from previous indications for marine waters samples (Baker et al., 2011). By considering both, it is noticeable that H_2O_2 is used in the vast majority of studies dealing with river water samples (94/107). Regarding sediment samples, about 60% of papers (54/91) applied OM treatment in their studies. H_2O_2 methods were dominant as for water samples with 94% of studies used this solution (51/54). The protocols with only H_2O_2 use most often a concentration of (30%) but with variations in the temperature (20–75°C) and the duration (2–72 h). H_2O_2 alone was used in 24/91 studies, Fenton was applied in 21/91 studies, and H_2O_2 was combined with strong acids (e.g., H_2SO_4 and HNO_3) and strong base (i.e., KOH) in 6/91 studies.

This widespread use of H_2O_2 is already observed the early studies and remains true for 2021 (Fig. 3.4). It is in agreement with the encountered recommendations from the scientific community. Early studies favored Fenton reactions to basic H_2O_2 treatment for sediments and used both equally for water. Hurley et al. (2018a, b) showed that Fenton is an optimal protocol to extract plastic particles from complex and organic-rich matrices (e.g., soil and sludge) without damaging them. Not only it requires less time reaction, Fenton also effectively removed organic components including highly chlorinated aromatic compounds,

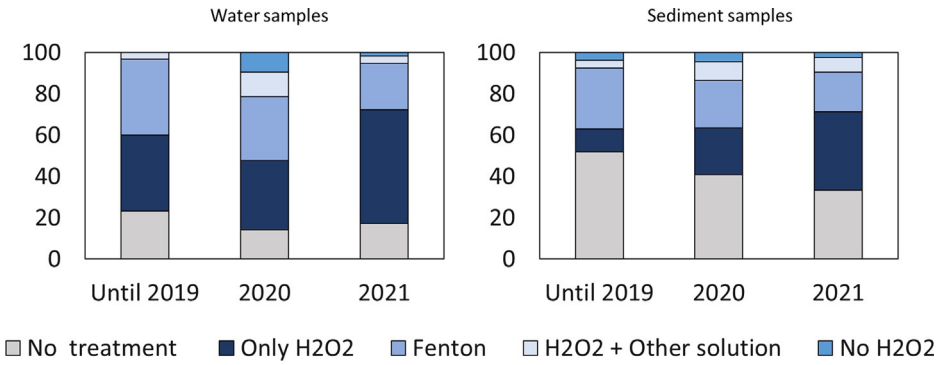

FIG. 3.4 Time evolution of methods used for organic matter removal.

which are normally recalcitrant in H_2O_2. There are some requirements to ensure the efficiency of Fenton reactions. For example, the pH of the reagents needs to be adjusted between 3 and 5, and the temperature should be monitored due to the exothermic nature of the reaction (Hurley et al., 2018b). Although Fenton reaction is more time-efficient and exhibits an improved OM removal, basic H_2O_2 treatment is frequently preferred. This is often due to its simplicity and cost-effectiveness. River samples can have a large variation on their OM content depending on the regional conditions and the seasonal/water flow variabilities. This leads to the fact that H_2O_2 treatment remains possible for certain studies while others require stronger treatments like Fenton.

Several protocols applying strong acid/base in association with H_2O_2 were tested. For example, Kaliszewicz et al. (2020) and Wang et al. (2020b) combined H_2O_2 with HNO_3 and HCl in their experiments, respectively. KOH and NaOH were added with H_2O_2 for treating samples in studies such Scherer et al. (2020) and Lisina et al. (2021). Strong acid/base (e.g., KOH and HCl) was also used in several studies without H_2O_2 to remove OM content (Abeynayaka et al., 2020). This method is often selected due to its high efficiency for OM removal and relatively low cost and fast reaction. It is however regularly mentioned that microplastics are easily degraded by strong acid/base solutions, rendering them not suitable for sample preparation (Avio et al., 2015; Catarino et al., 2017).

Strong bases and acids were mostly applied for nonH_2O_2 methods. They were much less common compared with H_2O_2 oxidation and Fenton reaction. KOH was the most common, showing high efficiency in extracting microplastics. However, this method is now known to cause damage to microplastics (Foekema et al., 2013; Dehaut et al., 2016). Similarly, strong acids such as hydrochloric acid (HCl) and nitric acid (HNO_3) were highly effective in removing OM but also destroy polymers, leading to degradation and melting of plastic particles (Cole et al., 2014). In general, alkaline and acid digestion is not recommended for treating samples in microplastic studies in order to ensure the preservation of plastic particles. In this context, enzymatic treatment, as a newly developed method, shows its potential. Löder et al. (2017) reported a removal efficiency of OM in sample matrix up to 97% without harming plastic particles. However, a series of enzymes required to break down different organic compounds leads the treatment to be of high-cost and time-consuming.

3.6.2 Mineral material removal

Prior to microplastic analysis, freshwater environmental samples generally undergo a mineral matrix removal in addition to the organic matter digestion. This step is particularly important for the analysis of sediment samples and freshwater samples that contain a significant amount of suspended solids. The mineral particles must be removed to enable microplastic analysis as they represent a minor fraction of the samples. Therefore, microplastic particles must be concentrated from a sufficient amount of samples to ensure representative results. Several methods have been proposed to isolate microplastics from the mineral fraction of samples: sieving and visual sorting (Gallitelli et al., 2020; Lucas-Solis et al., 2021), density separation (Hurley et al., 2018a; Kiss et al., 2021; Leslie et al., 2017), or extraction with oil (Crew et al., 2020; Lechthaler et al., 2021). About 60% (106/175) of the studies that focus on microplastic analysis in rivers use density separation, with 37 for sediments only, 26 for water only, and 43 for both. Density separation is performed by mixing the sample with a dense saline solution. For sediments, the saline solution is often directly mixed with the dried sample. For water, either solid salt is added to the sample volume or the sample is first filtered and the retentate is resuspended in the salt solution. To facilitate the resuspension of the retentate, the filter is optionally treated by ultrasonication (Johnson et al., 2020; Wang et al., 2020a). After stirring, the mixture is left to settle, plastics and other low density materials float in the supernatant, and mineral materials sink. A centrifugation step is in some cases added to improve the separation. Then, the supernatant is collected for filtration and analysis.

Several salt solutions have been used: sodium chloride NaCl ($d < 1.2\,g\,cm^{-3}$) (Frank et al., 2021a; Hoellein et al., 2017; Klein et al., 2015) in 49/106 studies, zinc chloride $ZnCl_2$ (d: 1.5–1.8 $g\,cm^{-3}$) in 31/106 studies (Eppehimer et al., 2021; Horton et al., 2017; Rodrigues et al., 2018), sodium iodide NaI (d: 1.5–1.8 $g\,cm^{-3}$) (Constant et al., 2021; Ta and Babel, 2020) in 6/106 studies, sodium polytungstate $Na_6[H_2W_{12}O_{40}]$ (1.4–1.8 $g\,cm^{-3}$) (Corcoran et al., 2020; Käppler et al., 2018; Siegel et al., 2021) in 5/106 studies, calcium chloride $CaCl_2$ (d: 1.4–1.5 $g\,cm^{-3}$) (Fraser et al., 2020) in only one study, and two solutions are used successively (Feng et al., 2021; Kapp and Yeatman, 2018; Zhou et al., 2021) in 7/106 studies.

The density of the separation solution must be adapted according to the density of the polymers targeted in the study. NaCl solution is most often used because it is cheap and environmentally friendly. However, NaCl solution has a maximum density of 1.2 $g\,cm^{-3}$, which does not allow the isolation of dense polymers such as PET and PVC (1.4 and 1.6 $g\,cm^{-3}$). This information indicates that nearly half of the studies having conducted density separation in river samples have a clear underestimation in certain polymers in their results. Both solutions $ZnCl_2$ and $ZnBr_2$ exhibit a density that can recover all plastic polymers (1.5–1.8 $g\,cm^{-3}$). These solutions have to be avoided in certain samples as they cause a reaction with carbonates and may produce a CO_2 release. The foam formed by the off-gassing can trap mineral particles and hinder their settling (Zobkov and Esiukova, 2017). For microplastic isolation, NaI provides a suitable density for the analysis of the main polymers found in the environment and does not produce a reaction with the matrix. In order to limit the cost and the quantity of waste, NaI solution can also be efficiently recycled after use by filtration and density adjustment by evaporation.

In more than half of the studies reviewed, the authors did not describe the method of recovering the supernatant after decantation. However, this is a tricky step as if the separation is carried out in a glass beaker, when pouring or vacuuming the supernatant, the particles remain stuck to the walls of the vessel and the decanted part is resuspended. Therefore, the separation must be repeated for the recovery of the supernatant to be effective (Amrutha and Warrier, 2020; Dikareva and Simon, 2019; Fang et al., 2021; Vaughan et al., 2017). To ease this step, the separation can be performed in separating funnels as described in Masura et al. (2015). However, this method is effective only for treating few grams of samples. To facilitate supernatant recovery, some research teams have developed valve devices (Coppock et al., 2017; Imhof et al., 2012). However, these devices require an extensive cleaning as all parts must be disassembled after each use. The device developed by Nakajima et al. (2019), composed entirely of quartz glass, addresses these technical issues. Indeed, this device can be custom-made and allows the separation of the supernatant from the decanted part without resuspending the mineral matter.

3.6.3 Sample contamination

To ensure the accuracy of empirical experiments, it is crucial to avoid contamination and have methods to quantify the level of contamination. Specific measures are recommended to reduce external contamination in samples, such as wearing cotton lab coats, working under a laminar flow box, never using plastic materials, covering samples constantly, and filtering all used solutions to remove plastics. Even when taking precautions, control samples are required to ensure the reliability of the samples.

In the corpus of this review, nearly 70% (120/175) of the studies conducted blank samples. They are either field blank or lab blanks. Field blanks are carried out to assess contamination during the sampling phase, which might come from the surrounding atmosphere or the application of a sampling device that contains some plastic components. In general, a clean filter/mesh or a clean container (e.g., Petri dish, jar, bottle) is exposed to the atmosphere during sampling to collect any airborne plastic contaminants, while a certain amount of deionized or Milli-Q water is run through the devices the same way as real sample to check the cleanliness of the systems (Lin et al., 2018; Kaliszewicz et al., 2020; Pan et al., 2020).

Compared to field blanks, lab blanks (called also sometimes procedure blanks) are much more common. Microplastic studies often require a long sample processing, and contamination can happen at any step during the process. Solutions having contact with samples and indoor air are often checked as contamination sources. Control samples will undergo the same treatment protocol as real samples to have an idea about contamination level.

About 35% of studies (42/120) that conducted control samples in their experiment detected no microplastics or negligible amount in the blanks (Irfan et al., 2020; Ji et al., 2021). In other studies, the contamination level is either reported independently with the results or used for data correction. One of the common correction methods is to subtract microplastics found in blanks from the result. This can be done based on the mean particle number or particle characteristics (i.e., polymer type, morphology, and color) (Bujaczek et al., 2021; Lin et al., 2021).

3.6.4 Microplastic recovery

Recovery rate tests for microplastic analysis are crucial to validate and verify the analytical methods used and facilitate cross-comparisons between studies (Way et al., 2022). The principle of recovery rate testing is to spike a sample with a known quantity of polymer particles and assess the efficiency (in %) of a method (or suite of methods) via the reverse evaluation of the loss (numerically or by weight) of the spiked microplastics. Often also called spiking tests, recovery tests are usually applied for the microplastic extraction processes in the laboratory, rather than during sampling.

There is an increasing interest in improving verification and validation for microplastic methods, and several studies focused on analytical procedures and conducted recovery tests. However, only 24/175 of the studies in the corpus reviewed in this chapter conduct recovery tests alongside their microplastic extraction procedures, and often, recovery rates are determined only for part of the steps. While contamination assessment seems well implemented in the scientific community, a validation of the recovery of microplastics is still only marginally deployed.

The most commonly used polymer types for recovery rate tests are PE > PP > PVC > PS > PA. A quarter of the publications include only one polymer type in the recovery test, while remaining use up to five different polymer types in their tests. Ideally, the spiked polymers are well characterized and represent the targeted microplastics expected in the samples in shape, polymer type, size distribution, density, color, origin, and chemical composition. This would allow to confidently determine the efficiency of methods for the respective samples. Though, regarding the complexity and variation of environmental matrices analyzed, methods used, and microplastics found in the environment, this is always overlooked.

3.7 How are the microplastic particles detected, quantified, and characterized?

The primary objective of all microplastic studies gathered for this chapter was to characterize and quantify the microplastic content of their samples. As a result, after the previously described steps, every study resorted to a microplastic identification method. In practice, the objective of such a step is to determine the number or mass of plastic particles in a given sample. In addition, the shape, size distribution, and chemical composition of the particles are characterized depending on the studies. In particular, the dominant polymers among the microplastics of a sample are often mentioned. In some studies, these analytical results may be converted or extrapolated into a microplastic flux in the river or into a sedimentation rate.

Like the other steps, microplastic identification practices evolved as the field advanced. Early studies mostly relied on visual analyses to identify plastic particles (Castañeda et al., 2014; McCormick et al., 2014). Later on, these visual methods either got coupled with some chemical characterization (Cheung et al., 2019; Horton et al., 2017; Hurley et al., 2018a) or were entirely replaced by a chemical characterization of microplastics (Dris et al., 2018b; Fan et al., 2021; Montecinos et al., 2021). In particular, Fourier Transform Infrared (FTIR) and Raman spectroscopy are largely used.

In the corpus used in this chapter 29/175 studies based their results exclusively on visual identification. Samples were observed under a microscope or a binocular magnifier. A determination key was used to assess whether particles were plastics based on their color, shape and texture. The particles considered to be plastics were then counted and categorized by shape: fragments, fibers, microbeads, etc. Such methods were first used because they were closest to taxonomic identification of plankton in marine biology, a research field from where many of the first research groups studying microplastic pollution came. However, such methods proved to be heavily biased in several ways. Visual cues used to confirm a particle as plastic or not depend on the experimenter and limit the possibility of comparing results between authors. Besides, visually identifying particles does not provide any information regarding their chemical composition. It is impossible to determine the polymers observed and thus the origin of the particles. As a result, it is advised that purely visual identification of microplastics should be abandoned from future peer-reviewed studies, especially regarding small particles. As observed in Fig. 3.5, even if it slightly decreased in proportion, studies with no chemical characterization keep being published and represent 17% of the papers in 2021.

In order to improve the bias of visual identification while avoiding the costs of spectral analysis, visual identification was coupled with a hydrophobic staining of particles in some studies. In particular, Nile Red staining is used in four studies (Crew et al., 2020; Ferraz et al., 2020; Prata et al., 2021; Valine et al., 2020). However, while Nile Red staining removes some of the bias caused by visual analysis, it can still cause some misidentification. Besides, no actual chemical identification of the particles is conducted, which prevents any interpretation of the microplastics potential sources. In five studies, Nile Red staining was combined with an FTIR analysis (Ji et al., 2021; Ta and Babel, 2020; Wang et al., 2018; Weber et al., 2021; Xia et al., 2021). In these studies, a subsample of particles identified through Nile Red staining was analyzed through micro-FTIR or ATR FTIR, to confirm the results or discuss the polymer types of the identified particles.

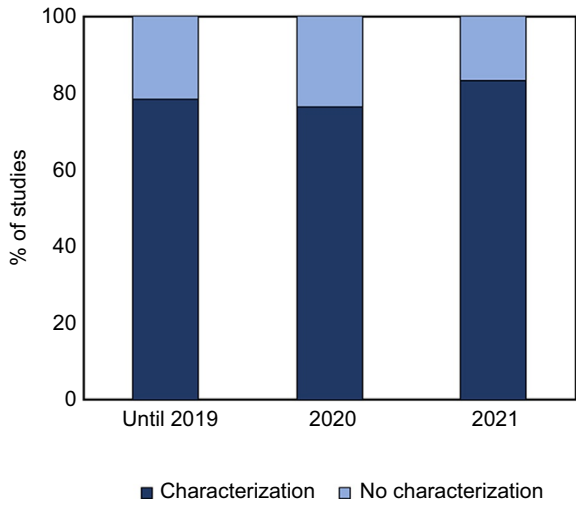

FIG. 3.5 Time evolution of the use of chemical characterization in studies.

3.7.1 FTIR

Fourier-Transform infrared spectroscopy is a form of infrared spectra acquisition method. While dispersive spectroscopy acquires spectral data over narrow wavelengths successively, FTIR spectroscopy allows the simultaneous collection of spectral data over a wide range. FTIR spectroscopy provides the absorption spectrum of a given material over wavelengths ranging from 4000 to 500 cm^{-1}, which corresponds to the near infrared. This absorption spectrum is specific to the material, and in the case of microplastic studies, a comparison with a library of already identified spectra is more often conducted. A matching score between the obtained spectrum and each spectrum of a library is calculated. If the highest matching score is higher than a certain value, the acquired spectrum is confirmed as being of the same material.

In the corpus gathered for this chapter, more than 60% of studies (110/175) relied at least partly on FTIR spectroscopy to characterize samples. Three main methods were used: Attenuated Total Reflectance (ATR), FTIR microspectroscopy (micro-FTIR), and mapping analyses coupled with micro-FTIR spectroscopy.

Attenuated Total Reflectance (ATR) spectroscopy is an acquisition mode for FTIR spectroscopy and allows a relatively quick analysis. During an ATR FTIR acquisition, the beam of infrared light passes through an ATR crystal in direct contact with the sample, at such an angle that it immediately reflects to the interface surface between the crystal and the sample. The resulting infrared spectrum is the absorption spectrum of the surface of the analyzed material, as the infrared beam typically only penetrates between 0.5 and 2 μm into the material. ATR spectroscopes are typically relatively cheap, but can only be used on particles large enough to be seen and manipulated without binoculars. As a consequence, this method relies always on a visual preselection. In this corpus, ATR-FTIR was used in around 30% (54/175) of all studies. One study used both ATR-FTIR and micro-FTIR for analysis, depending on the size of the particles.

In around 30% (57/175) of all studies, FTIR microspectroscopy (micro-FTIR) was used to analyze microplastics. In a micro-FTIR acquisition, the infrared signal is precisely focalized. This allows to both observe a sample like one would do on a microscope and to obtain an infrared spectrum of the sample. In the field of microplastic analyses, micro-FTIR spectroscopy can be used in two major ways. In the majority of studies, the samples are deposited and manually observed. Infrared spectra are then collected from visually or randomly selected particles. In five studies, however, micro-FTIR spectroscopy was not used that way but in an automated mapping analysis. In these studies, a pixelated map of the samples was produced, in which each pixel corresponded to one infrared spectrum. The maps then required an extensive posttreatment to identify plastic particles among the pixels.

In addition to the use of different appliances to collect infrared spectra, the way FTIR spectroscopy is used diverges among studies. In 31.4% (55/175) of all studies, only a subsample of all suspected microplastics was analyzed. The subsample is typically described by the authors to be representative of all identified particles, while being taken randomly. The use of such subsampling methods is usually justified as being more time-efficient than a more complete microplastic analysis. In addition to that, in 18.9% (33/175) of all studies, an ATR-FTIR was used to analyze a subsample of all suspected microplastics. It is likely for these studies that the authors did not have access to a micro-FTIR and thus could only identify the larger particles.

While better than a purely visual identification of microplastics, methods based on a subsampling of the suspected particles still present some human bias. The way particles are actually selected is rarely precisely described. Besides, several objectives exist in opposition to one another: the subsample has to be representative of both the whole sample and of all possible particle types found in the sample. In order to be representative of the whole sample, the subsample has to be a large fraction of the sample and to contain a high number of particles. Particles should also be randomly selected to avoid overestimating the fraction of certain polymer types. The main drawback of this method is the statistical representability when extrapolating the results of the subsample to the whole sample. This is particularly true as these subsamples are often very small.

In 23.4% (41/175) studies, instead of selecting a subsample, every suspected microplastic was counted and analyzed using FTIR spectroscopy. While analyzing every single particle takes more time than analyzing a subsample, it avoids the multiple human biases caused by the selection of a subsample. However, some bias remains in such methods. Indeed, samples are first observed under a regular microscope in order to select which particles to analyze. Because of this initial visual identification step, a risk remains to overlook a number of particles that would be microplastics. This method has the advantage of not causing an overestimation of microplastic concentrations but can lead to an underestimation.

Finally, as mentioned earlier, an extensive mapping of the samples was conducted using a micro-FTIR spectroscope in five studies, including one that deployed it for only a subset of samples. As such an analysis is almost entirely automatic, most experimenter-related bias is replaced by a constant machine bias, easier to reproduce, and even to redo later if the treatment method improves. Because it acquires much more infrared spectra than the number of microplastics, or even particles, in a sample, a mapping analysis takes a long time, typically several hours per sample. It also requires a long posttreatment, as the high number of acquired spectra prevents from verifying every single one manually. However, since part of this acquisition and posttreatment are automatic, the waiting time is not as limiting as active observation or counting could be.

While it appears less biased than other methods, the generalization of spectroscopic mapping analysis in the microplastic scientific community is limited by two factors. The first one is the machine cost. Micro-FTIR spectroscopes are expensive instruments, and imaging analyses require a specific array detector that is not always implemented in older instruments. The second limit of mapping analyses is the amount of data it generates. Each analysis generates large maps, which must be exported several times throughout the posttreatment. In order to compare or reproduce results, all data must be stored and available in online or offline servers. Moreover, the number of spectra generated (variable depending on the size of the maps and the spatial resolution, but generally more than 100,000) makes it impossible to manually identify the presence of microplastic spectra. Two of the five papers using automatic imaging identify the microplastic spectra using the software and the databases of the FTIR company. They are both from the same working group (Park et al., 2020a, b). The remaining three studies use the open-access software siMPle (old version called MPhunter) (Johnson et al., 2020; Mintenig et al., 2020; Scircle et al., 2020).

It is difficult to estimate the analytical size limit of all FTIR studies. It is generally not stated and difficult to identify as often a visual preselection is required. The latter does not have a clear-cut size limit. Typically, this method can target particles down to a few hundred

micrometers and gets less reliable the smaller the particles get. Studies will often consider their size limit as the sampling cutoff. Micro-FTIR spectroscopy with automatic imaging is the only exception as it has a size limit based on the pixel size of the image and is explicitly stated. In the corpus, it is of 25 µm (Johnson et al., 2020; Park et al., 2020a) or 20 µm (Mintenig et al., 2020).

3.8 Raman

Raman spectroscopy is a spectroscopic method used to acquire a spectral fingerprint of a material. While it provides similar information as infrared spectroscopy, it relies on a different principle, called Raman scattering. During a Raman acquisition, a source of monochromatic light (typically a laser in the visible light range) is directed toward the studied material. As the laser interacts with the material, its energy is shifted up or down. As a result, a Raman acquisition provides a continuous spectrum of that energy shift, around wavelengths (or wavenumbers) similar to that of infrared spectroscopy.

In the field of microplastic studies, Raman spectroscopy is largely used in the same way as FTIR spectroscopy: spectra are collected and compared to a database of reference spectra. However, some major differences remain between the two methodologies. Firstly, micro-Raman spectroscopy can reach a higher resolution than FTIR. Raman mapping or "point and click" acquisition methods have a theoretical pixel size of one or a few µm, much less than the pixel size provided by micro-FTIR.

However, Raman spectra acquisition is slower than FTIR. At least a few dozen seconds are necessary to optimize the signal of any spectrum, compared to less than 1 s for an FTIR acquisition. In addition, the 1 µm resolution of Raman spectroscopy makes it impossible to produce complete maps of a sample within reasonable timescales. Raman spectroscopy is also more sensitive than FTIR spectroscopy. In particular, Raman spectra can be highly affected by a material's fluorescence, which can make the spectra unreadable.

Nearly 15% (26/175) of studies in this corpus specifically mentioned the use of Raman analysis to characterize microplastics, 22 of which were published in 2019 or later (Fig. 3.6). Twelve of these studies only analyzed a representative subsample of all suspected microplastics and extrapolated their results. The other 14 studies characterized and counted every suspected microplastic. In one study, Raman was compared with FTIR spectroscopy (Sekudewicz et al., 2021).

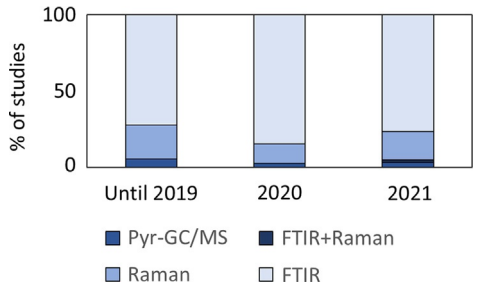

FIG. 3.6 Time evolution of the microplastic identification used in studies.

3.9 Py-GC/MS

ATR-FTIR, micro-FTIR, and Raman microspectroscopy are generally recognized as the reference methods for the characterization of microplastics in environmental samples. Indeed, the majority of studies use these approaches for the analysis of microplastics in water and river sediment samples. These spectroscopic analysis methods allow to obtain above a size limit of 1–25 μm, an estimation of the number of particles per unit of surface or volume. The mass of microplastics is sometimes determined from calculations integrating the number, shape, and density of particles. However, these approximations do not provide accurate mass concentrations and mass balances. To address these limits, Pyr-GC/MS can be used for the analysis of microplastics in environmental samples. This method was used for the qualitative (Campanale et al., 2020a; McCormick et al., 2016; Pojar et al., 2021) and quantitative (Käppler et al., 2018; Laermanns et al., 2021) analysis of microplastics in 6/175 of the selected studies. Pyr-GC/MS allows a molecular analysis of the polymers that compose plastics. As polymers are high-molecular-weight molecules that are not volatile, only their pyrolysis products can be analyzed by GC–MS. Some products are specific to their source polymers, which allows their unambiguous identification without size limitation.

In the majority of studies, Pyr-GC/MS has been applied on visually preselected microplastics in order to determine the nature of the suspected particles. However, as mentioned earlier in this chapter, visual identification of microplastics is largely limited by human biases. Campanale et al. (2020a, b), used pyrolysis to characterize microplastic polymers from river water samples and industrial preproduction plastic particles. About 3% of the particles in this study were analyzed by Pyr-GC/MS. Pojar et al., 2021 also performed this procedure for the analysis of 0.8% of selected particles from water and sediment samples. In these two studies, Pyr-GC/MS was applied only for the characterization of microplastics in order to provide a general overview of the types of polymers most commonly found in the samples. Laermanns et al. (2021) also used Pyr-GC/MS for the characterization of 6% of selected particles with a stereomicroscope, in addition they used an internal calibration quantification method for PE, PS, and PP. The applied quantification method was developed by Dierkes et al. (2019), microplastics are solubilized by pressurized liquid extraction with an organic solvent at high temperature (tetrahydrofuran THF at 100°C). The extract is then mixed with 200 mg of silica and 20 mg of this mixture is pyrolyzed after addition of poly(4-fluorstyrene) as internal standard. In all the previous studies, it is clear that the cost and time limits of Pyr-GC/MS cause that only a very small fraction of suspected particles could be analyzed.

Some studies did not proceed to single analyses of preselected particles but rather put full subsamples with a mixture of unknown particles (microplastics and natural organic and mineral particles). Quantification via the method of Dierkes et al. (2019), was also used in the study of Scherer et al. (2020). In this study, Pyr-GC/MS was applied for the quantification of PE, PS, and PP in the fine fraction of the sediment samples (20–125 μm) and in the fraction above (125–5000 μm). PS-d5 was used as an internal standard to correct for attenuation of the pyrolysis product signal caused by matrix effects. This use of Pyr-GC/MS without prior visual separation of particles should be preferred for the analysis of microplastics as it avoids the bias caused by the selection criteria. However, the use of solvent for polymer extraction does not seem to be a suitable option for studying all polymers, which are not soluble in an

organic solvent. Moreover, it involves extensive sample preparation, which is not recommended for the development of the method in Pyr-GC/MS. The advantage of this method is to be able to analyze solid samples, without the necessity of time-consuming preparation. For sediment samples, density separation of microplastics from the mineral fraction followed by digestion of the organic material may be adequate to concentrate sufficient quantities of microplastics for quantification.

Although recent studies on the application of Pyr-GC/MS are promising, there is still a lack of knowledge on the correspondence of the results with spectroscopic methods. This comparison work is needed to assess the advantages and limitations of each method as well as their complementarity. A study (Käppler et al., 2018) was interested in comparing μ-IRTF and Pyr-GC/MS spectroscopy methods for the analysis of microplastics in water and sediment samples. For this purpose, 27 particles suspected to be microplastics were selected (17 particles and 10 fibers) to be analyzed by both methods. Of these microplastics, 26 were detected as being composed of synthetic polymers by both methods, and 19 were recognized as the same polymer. External calibration runs were also performed for PE, PP, PET, and PVC to quantify five selected microplastics and compare their pyrolytic fingerprints with those of standard polymers. The pyrolytic fingerprints are similar between the microplastics and the standard polymers, and the calibration ranges were performed for masses ranging from 1 to 30 or 80 μg of polymer and gave an estimate of the mass of the five collected particles. The fibers analyzed individually were too small in mass to be quantified by Pyr-GC/MS. However, this is not a limitation as Pyr-GC/MS is not dedicated to the analysis of individual particles but of a mixture of microplastics isolated from the environmental matrix.

This comparison work confirms the high correspondence between the two methods but would require further investigation for the analysis of microplastics in water and river sediment samples. Pyr-GC/MS is a destructive method and does not provide information on the size of the plastic particles in the samples, but has the advantage of allowing rapid analysis. Thus, in addition to allowing precise mass balances to be established, Pyr-GC/MS could be a performing tool for identifying highly contaminated areas prior to a more extensive analysis using microspectroscopy.

3.10 Are there any fully comparable studies?

While it is often stated that used methods in various studies make them incomparable, it is interesting to look in detail to verify to what extent this is true. To accomplish this, the 130 papers that analyzed microplastics in river waters until 2021 were grouped and checked regarding their similarities in the following methodological elements: Sampling method (net vs bulk vs pump), mesh size of the sampling, solution used for organic matter treatment (ignoring further details such as concentration and temperature), solution used for density separation (ignoring further details such as device used), quantification instrument (Visual vs FTIR vs Raman vs Pyr-GCMS) and approach (preselection, random subsamples, imaging). After this process, it was impossible to find any group of more than two papers using the exact same method. For instance, two papers from different groups have both sampled with nets of 333 μm, used Fenton to treat samples, NaCl for density separation, and provided

concentrations based on visual counting (Campanale et al., 2020b; McCormick et al., 2014). However, if we consider more details, McCormick et al., conducted the observation with SEM microscope and McCormick characterized further their visual observation with Pyr-GCMS. Next to the identification approach, sampling is also a major cause for method differences. It is possible to find up to 13 papers with common methods if the sampling method and the mesh size of the net are overlooked. Even if some methods seem to be widely used (like H_2O_2 for sample treatment or FTIR for detection), this shows how it is very hard to find common ground to characterize microplastic pollution in rivers. This situation hinders considerably a full and complete understanding of the sources, impacts, and fate of these particles in the environment.

3.11 Summary of main challenges and guidelines

The exhaustive vision of the methodological practices in studies dealing with microplastics in rivers helps understanding the challenge that the scientific community has to overcome in order to improve the global understanding of this pollution. While it appears that various studies use different approaches, one of the difficulties faced in this work is the fact that information is often missing in the peer-reviewed papers. We provide here some practical recommendations. These recommendations appear to us as crucial, and should be considered by the whole community, both from scientists when publishing on one hand, and reviewers during the evaluation process on the other.

Based on the review, it appears now generally accepted to define microplastics as smaller than 5 mm (rather than smaller than 1 mm, which is still used). In order to not contribute to the general confusion, this definition should always be considered as the applied one. However, reality is more complex and even with an agreed upon definition, methods always present an upper and lower cutoff that are hard to accurately fix. As a consequence, studies need to always very clearly state the size limits of their methodology (both upper and lower) in order to make it easier for other studies to assess the comparability. This is the most sensitive point regarding all the recommendations presented in this chapter. Methodological size limits affect directly the observed results and cannot be overlooked in any attempt to compare data or apprehend the conclusions of a study. It is also important to consider clarifying the uncertainties and biases surrounding these limits as often they are not strictly limited.

The sampling step is the one presenting the most variability between studies. When trying to identify studies with fully comparable methods, the sampling was the main limiting factor. In addition to these differences, information is often missing in the publications. The sampled volume is often overlooked as an important data to provide, while it affects directly the representativity of the samples and should be stated.

Regarding sample preparation, the time and cost efficiency of H_2O_2 helped make this method the most frequently employed for organic material removal. Using the exact same solutions for organic material removal and density separation is not crucial and not always feasible as different rivers do not have the same type of content. However, should be completely avoided the use of: solutions that degrade plastic particles such as strong acids for organic material removal, and solutions with a density lower than plastics such as NaCl for density separation. This is important in order to conduct an exhaustive counting of

plastics. When not possible, studies should explicitly state which polymers can be targeted with their methods and which ones are not considered in the results.

It emerges from this corpus that spectroscopic analyses, in particular FTIR analysis, are becoming the dominant microplastic identification method. Because these methods provide a chemical identification of the particles, they are less biased than methods purely based on visual identification. However, the need for methodological standardization remains. While Pyr-GC–MS is currently not used in many studies yet, it is a promising method of focused analysis that could be coupled with spectral analyses in the future.

In most studies, FTIR analyses are conducted by comparing obtained sample spectra with wide libraries of plastic and nonplastic particles. The spectra used in such libraries play a large part in the polymer determination and can prevent different studies from being comparable. In order to improve the comparability of results, standardized libraries should be used among studies. While sampling plays a major role on the size (and therefore number) of microplastics identified, it is often known and considered by the scientific community when attempting comparisons among studies. The differences between spectroscopic databases for the identification of spectra is on the other hand overlooked while it can provide a large variability yet to be determined.

While it is understandable that not all labs can have an easy access to a spectroscopic method, purely visual microplastic identification presents a large human bias that prevents comparison between studies. Future studies using these methods should not be accepted if they attempt to quantify the totality of microplastics. Visual counting has been considered as acceptable and relevant only when considering large debris and/or man-made fibers (without any distinction between plastic polymers and other fibers such as rayon). While these topics are also very relevant, the scope should be clearly defined in the studies.

3.12 Conclusion

If we take the majority for each of the criteria described in this chapter, we can consider that the "average study" targets the water column when studying rivers, takes place in Asia, uses a net to sample water with an average cutoff of 330 µm, takes a volume of around 6500 L, uses H_2O_2 to remove organic materials, uses NaCl for density separation, makes blanks to verify contamination, does not carry out spiking tests, and uses µFTIR on a random subsample to analyze microplastics. If the community wanted to achieve a common method to be employed, this protocol would be the easiest one to generalize as these practices are the most widespread. However, it is clear that this protocol would not be ideal as, for instance, using a solution denser than NaCl would be advised, targeting microplastics smaller than 330 µm would be useful and switching to a full µFTIR mapping would be more reliable.

The introduction of this chapter took a citation from 2018 stating "it is still a long way until routine monitoring approaches are established." By adding more recent papers until the end of 2021, this statement remains completely true. Group efforts are absolutely required in order to start building a comparable database and state of art on the contamination of rivers by microplastics. This is crucial in order to obtain a good global overview on the impregnation levels of the environment with these particles, and further understand their sources, fate and impacts.

The main drawback preventing for a better understanding of this pollution, is the general tendency to consider "microplastics" as a general category to be targeted, quantified, and characterized in all studies dealing with topic. It is now more and more apparent that a model microplastic particle does not exist, as this pollution comes in a complex continuum of shapes, sizes, polymers and composition. More importantly, there is no single method able to target the full spectrum of microplastic particles. In the corpus reviewed here, and as presented in details along the chapter, all studies are able to quantify only a fraction of microplastics depending on the used method. However, these studies often state "quantifying microplastics in rivers" ignoring the missed fraction. Rather than focusing on achieving fully comparable methods, it is better to consider the necessity to have studies explicitly identify which fraction of microplastics they reliably target. The deployed methods need also to be in agreement with the aim and scientific objective of the studies. The main recommendation that stems from this work is that rather than pushing for a common method for all studies, they should be more required to disclose full and explicit information about their approach, targeted particles, and limitations.

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