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Highlights from a review of microplastics in marine sediments

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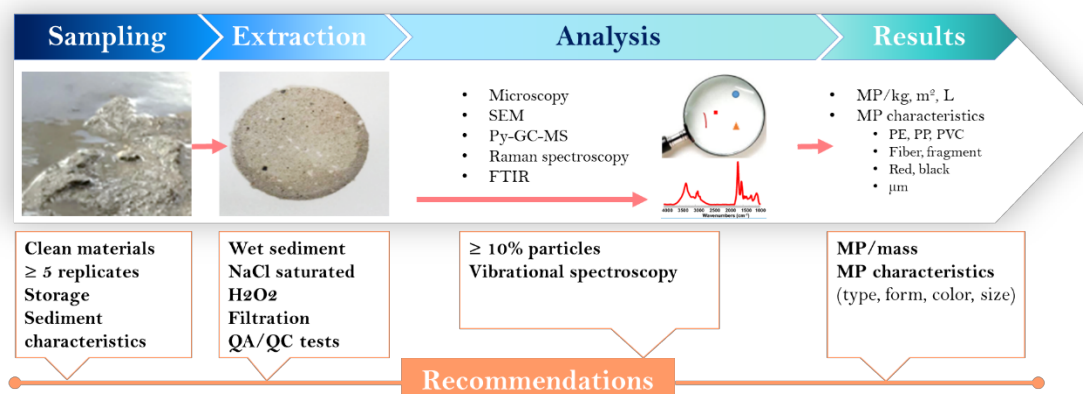
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Abstract

The ubiquity of microplastics (MPs) has now been demonstrated throughout Earth's geographic areas in both terrestrial and marine environments. Marine ecosystems are the end point of the plastic waste cycle, and marine sediments are increasingly considered to be a sink for plastic debris, with possible deleterious effects on seafloor ecosystems. However, the low concentration of MPs in a complex matrix such as marine sediment makes their reliable analysis difficult. MP concentration in marine sediments is usually determined by various extraction procedures followed by optical, spectroscopy or mass spectrometry techniques, and are therefore hard to compare. Therefore, reliable determination of MPs in sediment is a challenging task. Here we present a short review on studies dealing with analytical determination protocols and MP detection in marine sediments and discuss the advantages of the different techniques used. This analysis of the literature reveals that most of the 70 studies were carried out in European and Asian coastal environments. The use of NaCl saturated solution, hydrogen peroxide (H_2O_2) and Fourier transform infrared spectroscopy (FTIR) are by far the most-used techniques for the different steps of separation, digestion and identification, respectively. Based on this body of literature, we present recommendations and suggestions for future research in order to increase the reliability of results and to facilitate inter-comparison. The use of NaCl saturated and H_2O_2 solution is strongly recommended for the separation and digestion steps, respectively, whereas during the filtration step it is necessary to choose filter type based on the identification technique. More thorough investigation is needed to establish a systematic protocol for MP identification. A combination of techniques would permit to identify all items, and personal bias could be avoided if automatic identification was implemented. Nanoplastics (NP) occurrence in marine sediments is also discussed, although no data are available to date.

Graphical abstract:



I. Introduction

The discovery of plastic polymers began in the 1920s and 1930s and rapidly led to the invention of polyvinylchloride (PVC in 1920), polystyrene (PS in 1930), polyethylene (PE in 1933)¹, resulting in the exponential production of new manufactured products which were rapidly adopted by 20th century societies. Plastic production now increases by approximately 10 million tons each year, and reached 359 million tons in 2018, excluding production of polyethylene terephthalate (PET), polyamide (PA), and polyacryl-fibers². More than 8 billion tons of plastic have been produced since 1950³, half of which for single use items⁴. While plastic waste collection and treatment vary strongly between countries, vast quantities of plastic waste are being globally mismanaged or are tossed into landfills each year. Plastic dispersion into the environment is therefore of primary importance⁵. MPs are defined as plastic items smaller than 5 mm, whereas plastic items between 5 and 25 mm and > 25 mm are categorized, respectively, as meso- and macroplastics⁶. MPs are further classified into two size ranges including large MPs between 1 and 5 mm and small MPs of less than 1 mm⁷. For the classification of the lower size limit, there are several propositions: > 1 mm; > 20 μm ; > 1.6 μm and > 0.1 μm ⁸⁻¹¹. Although macro- and meso-plastics wreak dramatic deleterious physical damage including strangling or occlusion¹², MPs have a potentially higher capacity to be ingested, transferred into food webs, and finally to impact both organism physiology and ecosystem functioning due to their small size and high surface area. Two MP sources are identified including primary MPs that include items used in cosmetics as well as raw MP pellets¹³⁻¹⁵, and secondary MPs that originate predominantly from the fragmentation of larger plastic debris¹⁶. Numerous studies dealing with the detection and distribution of MPs in aquatic systems have been published in the last decade.

The presence of MPs in the environment has been reported from pole to pole and on all continents^{17,18}, from air, terrestrial waters, oceans, sediments, and biota¹⁹⁻³¹. This indicates that all Earth's surface compartments have already been affected by the injection of MPs. Numerous studies in recent years on (i) MP toxicity due to the polymer itself or to the additives or adsorbed pollutants released, and on (ii) fragmentation mechanisms, are proof of the attention currently being paid to MP environmental issues by the scientific community³²⁻³⁴. As the end-point of the plastic waste cycle, the marine environment has been widely studied. Around 10 million tons of plastic waste are dumped into the global ocean each year⁵. MPs have been found in seawater, in organisms ranging from zooplankton to fish, birds and turtles, in sandy and coastal sediments, as well as in seafloor sediments³⁵⁻⁴⁴. After reaching the ocean, many MPs sink in the water column after a change of density driven by physical,

chemical and biological interactions⁴⁵. Despite the fact that the sinking mechanisms of MPs in the marine environment are not yet fully understood, the majority of MPs by mass and quantity are found in sediments due to this change of density and/or to bio-interactions, and are subsequently found in high abundance in surface sediments (top 5 cm layer)⁴⁶⁻⁴⁹. However, there is a lack of conformity between studies concerning all steps of MP quantification in the sediment compartment: sampling, preparation, separation, extraction, identification and treatment of results. This study thus aims to review the various protocols used at each step when evaluating MPs in marine sediments, a compartment that can be likened to a large repository and reservoir of plastic debris. Recent reviews have focused on all sediment types (including lake, river and marine sediments)⁵⁰⁻⁵⁵. Based on 70 studies, we compared the various protocols used at each step and discuss their advantages and shortcomings in the aim of harmonizing them to lead to results that are more comparable across the global ocean.

II. Methodology

Marine sediments, including beaches, coastal and deep-sea sediments, make up the compartment most affected by MP contamination, and studies on this topic will be the focus of this review paper. The 70 studies were selected from international journals using the following keywords: “microplastic” and “marine sediment” on the Web of Science platform. All original papers including these two keywords were examined before the selection. The papers were published from 2004 to March 2020. Four studies (6%) were published in the 2004-2009 period, while 74% of the studies date from the 2015-2020 period. The papers come from 23 different journals, with most articles being published in the *Marine Pollution Bulletin*, *Environmental Pollution*, and *Science of the Total Environment* (27, 14 and 7 papers, respectively). Each study was reviewed carefully with particular attention given to methods of sample collection, MP extraction, MP identification and results reported. This critical review of this body of literature allows us to put forward recommendations and make suggestions concerning future research investigating MP contamination in marine sediments.

III. Results and discussion

III.1. Sediment collection

III.1.1. Study areas

We found that studies on MPs in marine sediments have been published in at least 70 articles, at a total of 813 locations on all continents, including Earth's poles (Figure 1). Areas studied are mainly in coastal environments, and the number of locations examined per study ranges from 1 to 72. It is noteworthy that this topic is paramount in Europe (mainly in the Mediterranean Sea and the North Sea) and in Asia, which together account for 80% of the total studies, while in South America the subject area has not yet been closely investigated. In recent years, Asia has become a hot-spot of plastic pollution, and 8 of the 10 world's worst countries in terms of plastic waste disposal are Asian, including the top three polluters, which are China, Indonesia and the Philippines⁵.

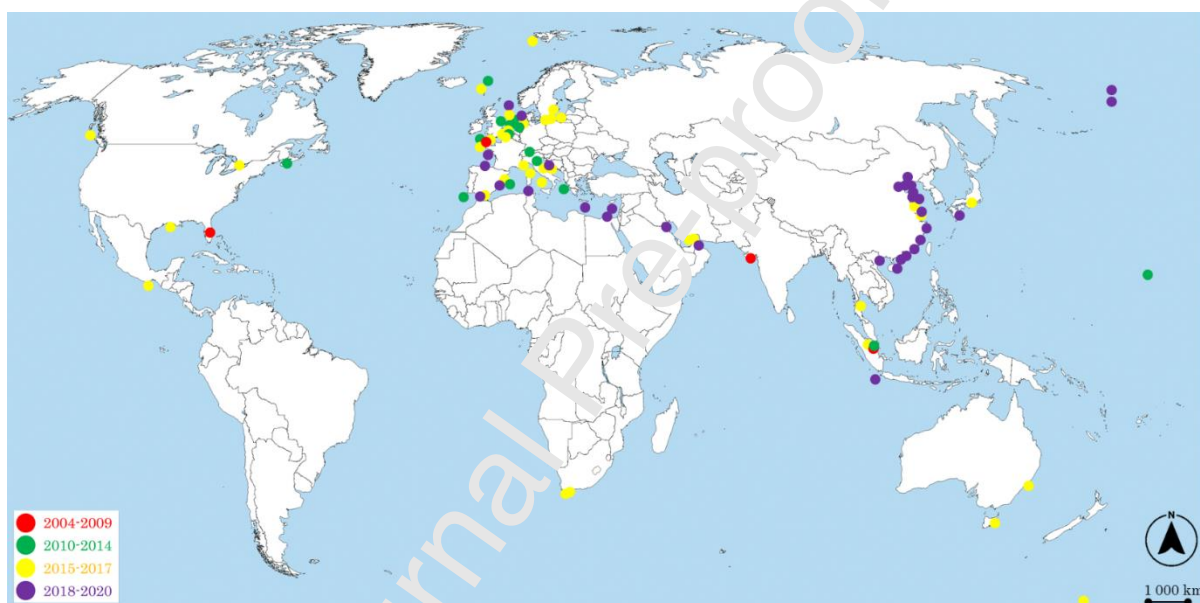


Figure 1: Study areas for MPs in marine sediments, reported since 2004.

III.1.2. Sampling and storage

Reports into open ocean bottom sediments (seabed, seafloor) represent 10% of studies, while the remainder of the studies focus on beaches and coastal areas. Sample collection protocols reveal a large diversity: depending on the type of sediment (seafloor, open ocean, coastal, beach) and on the research group, samples were collected with different numbers of replicates, with different surface collection areas and with steel utensils of different types. Indeed, seafloor MPs were usually sampled using equipment as diverse as box corer or Van Veen grabs, while beach and coastal–sediment collection was usually performed with quadrants, buckets, glass jars and sometimes with metal spoons. Sediment core samplers are appropriate for both sampling types. High quantities of MPs were found in the top layer of the

sediment (up to 7000 items per kg of dry sediment), and while deeper layers were much less contaminated by MPs (seven times less in sediments from 38-40 cm than from 0-2 cm depth)⁴⁸, they contain important information concerning both temporal trends and degradation mechanisms⁴⁹. Other factors were evaluated as potential drivers of MP distribution, such as wind driven accumulation on beaches, and proximity of waste disposal activities. Downwind areas seem to be more affected⁴², while human activities were revealed as high factors of MP contamination⁵⁶⁻⁵⁸. The number of replicates sampled in each study depended strongly on the characteristics of the study area. Table 1 presents information on sample collection of the published studies. The main differences in sample collection include the quantity of sediment sampled, the number of replicates, and the depth. Two methods for sample collection were presented by Hidalgo-Ruz et al. (2012)⁵⁹: bulk and volume-reduced sampling⁵⁹. Their paper describes the use of a sieving technique which permits to select the particle size during the sampling procedure. The first method (bulk sampling) refers to a procedure in which the whole sample is collected, a method frequently used for biota and sediment samples (including lake, river, sandy and marine sediment). Regarding the 70 studies selected, only two were related to samples sieved *in situ*^{86,88}. Volume-reduced sampling with different mesh sizes was generally used for water samples, since it permits to cover large areas. This method is also preferred for water samples, potentially because of the lower quantity of MPs in water, as compared to sediments. However, the choice of sampling method also depends on the study objective (particularly concerning the target MP size). Direct sieving on site is sometimes undertaken for beach sediment samples (lower water content) when the MP size of interest is greater than 1 mm.

TABLE 1. SAMPLE COLLECTION FOR THE STUDY OF THE THIRTEEN COUNTRIES.

<i>Sampling area</i>	<i>Type of environment</i>	<i>Material</i>	<i>Supplementary information</i>	<i>References</i>
<i>Tunisia</i>	Coastal sediments (5 locations)	Stainless steel spatula	3 squares (0.25 m × 0.25 m × 2-3 cm)	(60)
<i>Spain</i>	Coastal sediments (3 locations)	Core tubes	2 replicates × (30 cm × Ø3.5 cm) × 2 sites	(61)
<i>Canada</i>	Beach sediments (5 locations)	Split spoon corer	2 replicates × 20 cm	(62)
<i>Arctic</i>	Seafloor (9 locations)	Core sampler	3-6 replicates × (5 cm × Ø10 cm)	(63)
<i>Croatia</i>	Coastal sediments (10 locations)	Glass jars 1500 mL	3 replicates	(64)
<i>Scotland</i>	Intertidal (13 locations)	Glass jars 5 mL	3 replicates × 3 cm	(65)
<i>England</i>	Coastal sediments (6 locations)	Squares	5 squares (0.25 m × 0.25 m)	(42)
<i>Italy</i>	Coastal sediments (4 locations)	Vibrocorer/Grab	2 replicates × (0-50 cm ; 100-150 cm)	(43)
<i>USA</i>	Beach sediments (2 locations)	Core sampler	5 epibiotics × (5 cm × Ø5 cm) × 2 depths	(66)
<i>Hong Kong</i>	Seabed (4 locations)	Metal spade	6 replicates of top 4 cm, total 1 L	(44)
<i>Belgian</i>	Coastal and offshore sediments (20 locations)	Core/Van Veen Grab	1 kg/ 0.1 m ² sampling surface	(56)
<i>England</i>	Coastal sediments (3 locations)	Core sampler	3 replicates × (2 cm × Ø10 cm)	(67)
<i>Canada</i>	Beach sediments (3 locations)	Stainless steel spoons	250 mL (removed of top 5 cm)	(68)
<i>Germany</i>	Coastal sediments (3 locations)	Stainless steel spoons	6 replicates × (0.25 m × 0.25 m × 3 cm)	(69)
<i>Indonesia</i>	Coastal sediments (7 locations)	Grab	3 replicates × top 10 cm	(70)
<i>France</i>	Coastal sediments (9 locations)	Van Veen Grab	3 replicates × top 5 cm	(57)
<i>Germany</i>	Coastal sediments (2 locations)	Metal spoon	Top 2 cm (1.9 – 4 kg)	(71)
<i>Poland</i>	Bottom/beach sediment (9 locations)	Van Veen Grab/metal ring	5 replicates × (2.5 cm × Ø10 cm)	(72)
<i>USA</i>	Coastal sediments (3 locations)	Bucket	5-8 L	(73)
<i>Italy</i>	Coastal sediments (14 locations)	Bucket	2 replicates × 2 L (top 10-15 cm or 50 cm)	(74)
<i>Norway</i>	Bottom sediment (4 locations)	Van Veen Grab/metal spoon	3 replicates × 1 kg of top 1 cm	(75)
<i>Italy</i>	Beach sediments (2 locations)	Grid sample	3 replicates × (0.2 m × 0.2 m × 5 cm)	(76)
<i>Germany</i>	Coastal sediments (4 locations)	Metal spoon	3 replicates × 10 m ² of top 1 cm	(77)
<i>Lebanon</i>	Sublittoral sediments (3 locations)	Steel ring plates	Top 2 cm	(78)
<i>Netherlands</i>	Coastal sediments (15 locations)	Van Veen Grab	5 replicates × top 10 cm	(79)
<i>China</i>	Mangrove sediments (9 locations)	Stainless steel spatula	3 replicates × (1.5 m × 1.5 m × 3-4 cm)	(80)

Country	Location	Number of locations	Sampling method	Number of replicates	Depth of sample	Volume of sample	Reference
<i>Germany</i>							(97)
<i>Australia</i>	Subtidal	(42 locations)	Van Veen Grab/sample tube	70 mL of top 7 cm			(82)
<i>Germany</i>	Coastal sediments	(24 locations)	Van Veen Grab/metal spoon	1 L of top 5 cm			(83)
<i>Europe</i>	Beach sediments	(23 locations/13 countries)	Metal spoon	5 replicates × 100 g of top 5 cm			(84)
<i>North Sea</i>	Coastal sediments	(5 locations)	Nd	3 replicates of 5 g			(85)
<i>Portugal</i>	Beach sediments	(5 locations)	Quadrats	3 replicates × (0.5 m × 0.5 m) of top 2 cm			(86)
<i>Canada</i>	Beach sediments	(3 locations)	Quadrats	0.15 m × 0.15 m of top 3-4 cm			(87)
<i>Asia/Africa</i>	Coastal sediments	(11 locations/4 countries)	Core samplers	6 different depths			(48)
<i>Italy</i>	Seafloor sediments	(16 locations)	Van Veen Grab	4 replicates × (1 J can × 10 cm)			(88)
<i>Arctic Ocean</i>	Marine sediments	(7 locations)	Box corer (50 × 50 × 65 cm)	1 kg of top 5 cm			(89)
<i>Ross Sea</i>	Marine sediments	(11 locations)	Van Veen Grab	3 replicates × 0.18 m ²			(90)
<i>Iran</i>	Intertidal at high tide	(5 locations)	Stainless steel spoon	2 replicates × (1 m × 1 m × 5 cm)			(91)
<i>Iran</i>	Coastal sediments	(5 locations)	Stainless steel spoon	3 kg of (1 m × 1 m × 1-2 cm)			(92)
<i>Iran</i>	Littoral sediments	(5 locations)	Stainless-steel shovel	3 replicates of top 5 cm			(93)
<i>South Africa</i>	Coastal sediments	(21 locations)	Nd	Top 5 cm			(94)
<i>Singapore</i>	Beach sediments	(7 locations)	Nd	3 replicates of 1 kg (top 1 cm)			(11)
<i>Singapore</i>	Intertidal mangroves	(7 locations)	Stainless steel spatula	3 replicates × (1.5 m × 1.5 m × 3-4 cm)			(95)
<i>Germany</i>	Marine sediments	(3 locations)	Stainless steel spatula	3 kg of top 3 cm			(96)
<i>China</i>	Seafloor sediments	(53 locations)	Box corer/bottle samples	3 replicates of top 5 cm			(97)
<i>France</i>	Coastal sediments	(3 locations)	Box corer/Steel spatula	3 replicates × (0.5 m × 0.5 m × 10 cm)			(98)
<i>India</i>	Intertidal sediments	(12 locations)	Stainless steel scoop	5-10 kg of top 5 cm			(99)
<i>Mexico</i>	Beach sediments	(9 locations)	Nd	1-6 replicates			(100)
<i>Kuwait</i>	Beach sediments	(44 locations)	Squares	3 replicates × (30 cm × 30 cm × 5 cm)			(101)
<i>Europe</i>	Seabed sediments	(29 locations/6 seas)	Core/Van Veen Grab	Top 1 cm			(102)
<i>Germany</i>	Beach sediments	(3 locations)	Stainless steel spatula	1-4 replicates × 500 mL of top 1-2 cm			(103)
<i>China</i>	Coastal sediments	(8 locations)	Box grab	Top 5 cm			(104)
<i>England</i>	Coastal sediments	(17 locations)	Trowel/Grab	5 replicates × 250 mL			(105)
<i>Hong Kong</i>	Coastal sediments	(4 locations)	Ekman dredge sampler	3 kg of surface			(106)

Country	Location(s)	Sampling Method	Sample Size	Number of Samples	Reference
Belgium	Coastal sediments (7 locations)	Metal spoon	6 replicates × (0.5 L of top 5 cm)	(108)	(107)
Europe	Coastal sediments (6 locations/3 countries)	Metal spoon	6 replicates × (0.5 L of top 5 cm)	(108)	(107)
Japan	Estuarine sediments (1 location)	Glass petri dishes	3 habitats × (60 mL of 50 cm ²)	(109)	(108)
Italy	Superficial sediments (10 locations)	Box corer	2 replicates × top 5 cm	(110)	(109)
China	Coastal sediments (12 locations)	Grab sampler	3 replicates × (32 cm × 20 cm × 15 cm)	(58)	(110)
China	Marine sediments (17 locations)	Box corer/Stainless steel spatula	0.5 kg of top 3 cm	(111)	(111)
China	Coastal sediments (13 locations)	Steel frame (25 × 25 cm)	3 replicates × (0.1 kg of top 5 cm)	(112)	(112)
USA	Intertidal sediments (7 locations)	Quadrats (25 × 25 cm)	12 replicates of top 10 cm sediment	(113)	(113)
Australia	Estuarine sediments (7 locations)	Core sampler	Different depths	(49)	(114)
Europe	Seabed sediments (16 locations/4 seas)	Core sampler	Top 1 cm of ∅ 10 cm	(114)	(114)
China	Marine sediments (25 locations)	Core sampler	2 replicates × top 1 cm	(115)	(115)
China	Coastal sediments (28 locations)	Core sampler	2 replicates × 0.25 kg of top 5 cm	(116)	(116)
China	Marine sediments (72 locations)	Box sampler	3 replicates × top layer sediment	(117)	(117)
China	Marine sediments (14 locations)	Van Veen Grab	0.6 kg of top 10 cm	(118)	(118)
China	Marine sediments (19 locations)	Box corer	0.5-1 kg of top 5 cm	(119)	(119)
Russia	Bottom sediment (7 locations)	Rectangular dredge	10 L	(120)	(120)

Nd (not determined), ∅ (diameter)

Immediately after sampling, sediment samples are usually transferred into glass containers (bottles, jars), although plastic bottle storage has also been reported. They are then transported back to the laboratory at cool temperatures (*i.e.*, kept in an ice box)^{44,71}, and are usually stored at cold temperatures in the dark, *i.e.*, -18 °C.⁹¹⁻⁹⁴ Storage duration before analysis was also variable, ranging from a few hours to several months. While none of the studies reported a degradation of MPs during transport and storage, high biofilm growth was observed during storage at room temperature⁶⁸.

III.1.3. Sampling and storage recommendations

Sediment collection is the most important step when gathering representative data at each sampling site. An adapted sampling strategy must be considered, taking into account the selection of the sampling sites, the number of replicates, and the distance between samples and replicates. Studies on MP distribution (as a discontinuous variable), require the collection of at least five replicates at each location, with a minimum distance of 100 m between them^{121,122}. Clean steel tools (washed and rinsed with Milli-Q water) are strongly recommended for sediment sampling. Sediments should be preserved in clean glass containers, placed at cold temperatures (around 4 °C) and be rapidly transported back to the laboratory. Storage temperatures must be respected until analysis. In addition, we suggest that all sample information, for example, location coordinates, area covered, volume and mass collected, depth and sediment characteristics (such as water content, organic matter content, size distribution) should be gathered and reported in order to allow comparison with other studies. It should be noted that the transport and storage of sediment samples for subsequent analysis of MPs is similar to conditions required for organic compounds, which are subject to possible degradation by bacteria or to contamination by storage materials^{123,124}. It is therefore preferable to store these types of samples at -20 °C in glass or metal recipients.

III.2. MP Extraction

Detection and quantification of MPs from sediment using physical or optical techniques requires preliminary steps of preparation including digestion, separation and isolation. Different reagents, materials used in each step are summarized in Table 2.

Table 2. Comparison of reagents/materials used on mainly operations for MP extraction in marine sediments

Operation	Reagent or material	Advantages	Drawbacks
Digestion	H ₂ O ₂	Inexpensive, availability Largest used, data comparable	Instability Loss of MP color observed Boil intensely at high temperature Adding slowly due to gas bubbles during heated
	H ₂ O ₂ and Fe ²⁺	Fast and efficiency MP characteristics preserved	Sharing drawbacks with H ₂ O ₂ solution Precipitation possible
	Enzyme	Highly efficient No damage to sensitive polymers	Time consuming Complexity, pH required
Separation	NaCl saturated	Availability and low price Largest used, data comparable Green method to the environment	Loss of MP possible due to lowest density
	ZnCl ₂	High recovery	Expensive Hazardous to operator and environment
	NaI	High recovery Re-used possible	Expensive Sensitive to pH
Isolation	Hand sorting	Simple and easy to work	Time consuming, experiment required Limited on MP large size
	Sieving	Rapidly Easy to clean and reused	MP size range still limited Loss of small MP Manually required later
	Filtration	Highly MP retained Diverse of filters are available Largest used, data comparable	Depending strongly to digestion and separation step Filter type must be defined priory

The H₂O₂ solution was most used for organic matter digestion while the NaCl solution was predominant in separation step. Both solutions permit to have data comparable to most of results reported. Filtration technique displayed best results to avoid small MP losses.

III.2.1. Sediment pretreatment

Quantities of sediment sample collected vary drastically among studies (Table 1). Generally speaking, only a portion of a sediment sample is used for MP analysis, depending on the volume collected, and pretreatment including sample homogenization, sub-sample selection, drying and sieving¹²², is therefore necessary prior to MP extraction.

a. Homogenization

homogenization of samples aims to obtain uniformity so as to ensure that the sub-sample selected for analysis is representative of the entire sediment sample. Ten percent of the 70 studies selected mention this preparatory step. Of these, only two studies used a method involving mixing and stirring^{58,120}. Once the sediment sample reaches room temperature, homogenization can be obtained using clean materials (*i.e.*, stainless steel spoons). Due to the heterogeneous distribution of MPs in the sediment,

homogenization is a crucial preliminary step. The sample is then divided (by splitting or sub-setting). The mass chosen for MP analysis (Table 1) depends on the objective of the study and the expected MP concentration.

b. Drying

Sixty percent of the studies were performed on dry sediment, while forty percent worked with wet sediment. Sediment drying provides a precise measurement of the quantity of MPs. Several techniques have thus far been adopted for drying the sediment matrix, with different advantages and drawbacks. First, the freeze-drying technique was reported in three studies^{48,79,106}, and usually involved exposing sediments to very cold temperatures (-50 °C or even down to < -100 °C) and very low pressure for durations ranging from a few hours to several days, depending on the quantity of sediment and the depth of the sediment layer. Second, another sediment drying method was reported in 26 studies (37%): this requires the heating of the sample to temperatures ranging from 50 to 80 °C for durations ranging from 16 to 72 hours, depending on the sediment composition and, more generally, on the practices defined by the working groups based on their own experience. A third method, involving drying in the air and sun, was also reported in a few other studies^{60,100-104}. The advantage of this latter method is to prevent MP degradation. However, its utility is limited to low water (<20%) content samples. Among these three drying techniques, freeze-drying is less used because of the need for more expensive apparatus, despite the fact that a porous sediment is obtained. With the use of hot-temperature drying (> 60 °C), an additional milling step is necessary if sieving is to follow. Note that sediment milling may also lead to the fragmentation of MPs, although such bias was not reported. Similarly, thermal/sun treatments for drying sediment may provoke the thermo-oxidation of MP particles, and therefore affect subsequent infra-red spectra, particle density, or other wear/hiding indicators⁴⁵.

c. Sieving

The operation of sieving is used to eliminate matrix particles and allows to obtain MPs of a specific size range. Approximately half of the studies (36/70) omitted a sieving step, while the other half applied different cutoffs, ranging from 25 µm to 5 mm (metal or nylon sieves). The sub-sieving of sediment samples helps to determine MP concentration in each size class, therefore several sieve sizes may be used to fraction the sediment particles into different size categories^{61,82}. This technique is highly efficient for MP fragments and pellets, but not for fibers or filaments. For example, a MP fiber exceeding 2 mm in length persisted after sieving using a 1 mm mesh⁹⁸. Sieving may thus be misleading, and furthermore, may be a source of contamination. However, taking into account the size definition of MPs, an initial sieving step at 5 mm seems necessary for the removal of larger items, while a second sieving at 1 mm is necessary to separate small and large MPs.

III.2.2. Digestion

The digestion step aims at removing the natural organic matter (NOM) from sediment samples. Indeed, the presence of organic matter hinders the filtration step and may lead to misidentification of

plastics. However, this step may also lead to the degradation (oxidation) of MP particles. Surprisingly, nearly 70% of studies did not include this step very likely due to the low organic matter content of the samples, involving a final filter clean enough for running the following steps.

Among the 70 studies, different reagents for the elimination of NOM were used, predominantly H_2O_2 (n=14), followed by a mixture of H_2O_2 with ferrous ion (Fe^{2+} , Fenton's reagent; n=6) and enzymes. Hydrogen peroxide (H_2O_2) is an oxidizing compound, which is used not only for sediment samples but also on biota and surface water, since it is inexpensive and easy to work with^{127,128}. In general, a concentration of 30% (w/w) was used, while duration ranges were reported from 12 hours (overnight) to a week, depending on the organic matter content.⁴⁹ A volume of 150 mL of H_2O_2 solution was added to 10 grams of sediment in Mathalon and Hill study, while only 5 mL were used for 50 grams of initial sediment in Zhao et al.^{87,117}. H_2O_2 seems more appropriate for sediment samples than acid or hydroxide reactants, although it also presents drawbacks such as instability. Furthermore, H_2O_2 was reported to discolor PA, PC and PP (> 1 mm) after 1 week⁹⁶. It should also be noted that this compound boils intensely when heated above 75 °C¹²⁹. Strong differences were described depending on the volume of H_2O_2 used for sediment samples. These divergences can be explained by the protocol used. Indeed, Mathalon and Hill (2014)⁸⁷ added H_2O_2 directly to the sediment matrix, whereas Zhao and co-authors (2018)¹¹⁷ conducted a separation step before the addition of the digestion reactant. Fenton's reagent (a mixture of hydrogen peroxide and ion Fe^{2+}) was first suggested by Masura et al.¹²⁹. These authors reported the use of 20 mL H_2O_2 30% with 20 mL Fe^{2+} 0.05 M for the removal of organic matter in water, beach and seabed samples. This reagent was more frequently used in the more recent articles. Its main advantage is that it reduces the digestion time to less than one hour⁸².

Enzymatic digestion in sediment samples was also reported, involving three different enzymes including protease, cellulose and chitinase¹²². It should be noted that single enzymatic digestion was reported only once, whereas a multi-digestion (enzymes and H_2O_2) procedure was used by Lorenz et al.^{75,83} This method was reported to be highly efficient (> 98%) for the removal of organic matter using a variety of materials and chemical products and undergoing three principal steps of MP extraction (Figure 2, Table 3). The main advantage of enzymatic digestion is that there is no damage to sensitive polymers such as Nylon and polyester fibers^{125,126}. However, this method is complex due to i) the use of surfactants for increasing the contact with enzymes, ii) the use of different enzymes, and iii) the use of buffers for pH adjustment. This method is therefore less often employed for sediment samples.

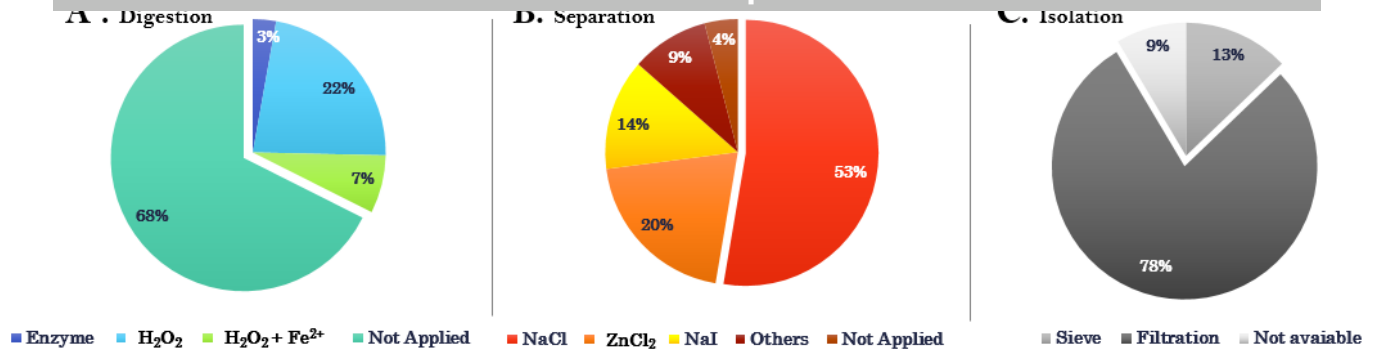


Figure 2: Reagents and materials used for MPs extraction in sediments (n=70), steps corresponding to digestion (A), separation (B) and isolation (C).

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Table 3: Overview of extraction processes for the study of MPs in sediments.

TYPE	SIEVE (SIZE IN MM)	DIGESTION (REAGENTS)	SEPARATION (SOLUTION, DENSITY)/(OPERATION)	FILTRATION (NATURE/POROSITY)	PROCEDURE RECOVERY (%)	REFERENCES
DRY	No	No	NaCl (Stirring 5 min)	Glass filter, 1 µm	Nd	(60)
DRY	Yes (2, 1, 0.5, 0.25, 0.125, 0.063)	No	H ₂ O (Shaking 15 min)	N.A	Nd	(61)
DRY	Yes (5, 6, 2, 0.063)	No	Na ₂ WO ₄ , 1.5 (stirring 2 min)	Paper filter, 2 µm	Nd	(62)
DRY	No	No	ZnCl ₂ , 1.7-1.8 (Stirring 35-60 min)	Steel filter, 20 µm	Nd	(63)
DRY	Yes (4.2, 1, 0.063)	No	NaCl saturate (agitated 2 min)	Paper filter	Nd	(64)
WET	No	No	NaCl saturate (Stirring 30 s)	Glass filter 0.7 µm	Nd	(65)
WET	No	No	NaCl saturate (Stirring 30 s)	Glass filter	Nd	(42)
DRY	Yes (4.2, 1, 0.063)	No	NaCl saturate (agitated 2 min)	Paper filter	Nd	(43)
DRY	Yes (4.2, 1, 0.5, 0.25)	No	NaCl, 1.2	N.A	Nd	(66)
WET	Yes (5, 0.3)	H ₂ O ₂ +Fe ²⁺	ZnCl ₂ , 1.6	Sieve 300 µm	Nd	(44)
WET	No	No	NaCl saturate (Stirring 5 min)	Sieve 38 µm	69-98%	(56)
WET	No	No	ZnCl ₂ , 1.5 (Stirring 5 min)	Nylon mesh 30 µm	92-98%	(67)
DRY	Yes (4.75, 1, 0.5)	No	Canola oil (Settle 2 min)	Polycarbonate, 1 µm	92-99%	(68)
DRY	Yes (1)	No	NaCl 1.2 + NaI 1.8	Nitrocellulose 0.45 µm	>91%	(69)
DRY	Yes (12 fractions)	No	NaCl, 1.2 (Stirring 10 min)	Paper filter, 0.45 µm	Nd	(70)
WET	No	No	NaCl 1.2+ Na ₂ WO ₄ 1.56	Glass filter 1.6 µm	100%	(57)
WET	No	No	NaCl 1.2 shaken manually	Nitrocellulose 0.45 µm	80-100%	(71)
WET	No	No	NaCl 1.2 (Shaking 2 min)	Steel sieve 45 µm	High efficiency	(72)
WET	No	No	NaI 1.425 (Stirring vigorously)	Polyester filter 0.25 mm	Nd	(73)
DRY	Yes (4.2, 1, 0.063)	No	NaCl saturate (agitated 2 min)	Filter 10 µm	Nd	(74)
WET	No	Enzymes	ZnCl ₂ , 1.7 (centrifugation 1000 x 25 min)	Steel filter 30 µm	Nd	(75)
WET	No	No	ZnCl ₂ , 1.6-1.7	Paper filter, 0.3 µm	Nd	(76)
WET	No	No	NaCl saturate (Stirring 10 min)	Glass filter, 0.7 µm	82%	(77)
WET	No	No	ZnCl ₂ , 1.8 (Stirring 5 min)	Glass filter	Nd	(78)

DRY	No	No	NaCl (Stirring vigorously)	Glass filter 0.7 µm	Nd	(97)
DRY	Yes (5)	H ₂ O ₂	HCOOK 1.5 (Settled overnight)	Glass filter 1.2 µm	Nd	(80)
DRY	No	H ₂ O ₂	ZnCl ₂ 1.5	Cellulose nitrate 1.2 µm	Nd	(81)
WET	Yes (7 fractions)	H ₂ O ₂ + Fe ³⁺	NaI 1.7 (centrifugation 3500 x 5 min)	Polycarbonate 1.2 µm	Nd	(82)
WET	Yes (0.5)	Enzymes + H ₂ O ₂	ZnCl ₂ 1.7	Steel filter 20 µm	Nd	(83)
				Al ₂ O ₃ 0.2 µm		
DRY	Yes (5)	No	NaCl (centrifugation 900 x 2 min)	Paper filter, 0.45 µm	Nd	(84)
DRY	No	No	Nile red, ZnCl ₂ 1.37 (centrifugation 3900 x 5 min)	Al ₂ O ₃ 0.22 µm	85-98%	(85)
WET	No	No	NaCl (Stirring vigorously)	Glass filter, 1 µm	Nd	(86)
DRY	No	H ₂ O ₂	NaCl (Stirring 2 min)	Nitrocellulose, 0.8 µm	Nd	(87)
DRY	Yes (5, 0.315)	H ₂ O ₂	NaI 1.6 (centrifugation 2000 x 10 min)	Nylon mesh 315 µm	93%	(48)
WET	Yes (1)	No	N.A	N.A	Nd	(88)
DRY	No	No	KI 1.7 (Stirring vigorously)	Glass filter, 0.7 µm	68-98%	(89)
WET	No	No	N.A	N.A	Nd	(90)
DRY	Yes (4.75, 0.025)	No	NaCl 1.2 + NaI 1.8 (Stirring vigorously)	Nitrocellulose 0.45 µm	Adapted Nuelle <i>et al.</i> , 2014	(91-93)
WET	Yes (0.065)	No	NaCl saturate (Stirring vigorously)	N.A	Nd	(94)
DRY	No	No	NaCl 1.2 (hak 200 x 1 min)	Paper filter, 1.6 µm	Nd	(111)
DRY	Yes (0.063)	No	NaCl 1.1 + Tween80 (shaking 200 x 1 min)	Paper filter, 1.6 µm	55-72%	(95)
DRY	Yes (1, 0.025)	H ₂ O ₂	NaCl 1.2 + NaI 1.8 (Stirring vigorously)	Nitrocellulose 0.45 µm	68-99%	(96)
DRY	No	H ₂ O ₂	NaCl 1.2 (Stirring manually 2 min)	Glass filter	Nd	(97)
DRY	Yes (1)	No	Water (centrifugation 500 x 5 min)	Nitrate cellulose 12 µm	83-100%	(98)
DRY	Yes	No	NaCl 30% (Stirring 1-2 h)	Glass filter	Nd	(99)
DRY	No	H ₂ O ₂	ZnCl ₂ 1.58	Nitrocellulose 1.2 µm	Nd	(100)
DRY	Yes (2, 1, 0.71, 0.5, 0.25)	No	NaCl saturate (Stirring vigorously)	Glass filter	Nd	(101)
WET	No	No	NaCl 1.2 (Stirring 30 s)	Glass filter	Nd	(102)
DRY	No	No	CaCl ₂ 1.3-1.35 (Settle overnight)	N.A	20-100%	(103)
WET	Yes (0.33)	H ₂ O ₂	NaCl 1.2 + ZnCl ₂ 1.5	Nylon filter 20 µm	Nd	(104)
WET	No	No	NaCl saturate (Stirring 30 s)	Glass filter	Nd	(105)

III.2.3. Separation

MPs must be separated from the sediment particles within the sediment matrix. Practically, sediment samples cannot be filtered because of the high quantity of sediment particles compared to MPs. A density separation step is thus usually performed (93% of the studies) using solutions of different densities. The use of a dense solution (e.g., KI, NaI, ZnCl₂, NaCl, etc.) allows to separate sediment particles (mean density 2.65 g cm⁻³) from MPs that are less dense than the chosen solution⁵⁹. The authors most often recorded plastic density values ranging from 0.8 to 1.4 g cm⁻³.

Three solutions are mostly used for density separation: sodium chloride (NaCl), zinc chloride (ZnCl₂) and sodium iodide (NaI). Densities reported for these solutions are 1.18-1.20, 1.37-1.80, and 1.43-1.80 g cm⁻³, respectively (Table 3). NaCl solution has less variation considering its density value, which explains why it is often used at saturation, which is around 352 g L⁻¹ (w/v) at 20 ° C. Only two studies used NaCl solution at lower concentration (140 g L⁻¹)^{60,86}. Density was more often reported than concentration units, but these values are convertible depending on temperature. The main advantages of NaCl utilization are its availability and low price. The shortcoming of NaCl is its low density, enabling to recover only some types of plastic polymer present in the environment (eg. PE, PS-E, PA, Kedzierski et al. 2017)¹³⁰. The use of denser solutions, such as ZnCl₂, NaI, CaCl₂, Na₂WO₄, and KI allows to recover denser plastic polymers, such as PVC (d=1.16-1.58 g cm⁻³), PET (d=1.37-1.45 g cm⁻³) and some fluoropolymers (d= 1.7-2.2 g cm⁻³) (Kedzierski et al. 2017)¹³⁰, in addition to other particles from the sediment which may potentially interfere with the visual determination during the following step. However, these solutions also present some drawbacks, for example ZnCl₂ is known to be a hazardous compound, CaCl₂ is very viscous and NaI is expensive and sensitive to pH less than 6.5¹³⁰. Kedzierski et al.¹³⁰ developed a protocol to re-use NaI up to 10 times in order to lower the overall cost. Sedimentation is subject to complex processes, particularly for small particles which are influenced by surface tension, physical and chemical properties, during which MP particles may interact rapidly with proteins, ions, micro-organisms, pollutants, leading a novel buoyancy to the aggregates that include MPs. The recovery of all MP types thus remains a difficult methodological challenge.

Many types of laboratory recipients were used for the MP separation steps, such as funnels, jars, Erlenmeyer flasks, beakers and tanks. All were made of glass, which is crucial when studying MPs. Surprisingly, some plastic equipment occasionally figures amongst the materials used, for example, centrifuge tubes made of PP or PTFE, a Sediment Microplastic Isolation (SMI) made of PVC, or an elutriation column made of PVC^{67,107}. Given the breakdown of plastic materials, the use of these materials must be avoided for MP studies. Although these plastics are considered to be stable, Haave et al. recently detected Teflon and silicone when using a MicroPlastic Sediment Separator (MPSS) for MP separation⁷⁵. MPs were separated principally using three mechanisms: flotation, elutriation and fluidization-flotation^{96,105,107-108}. However, as outlined above, elutriation columns and other separators (MPSS, SMI) are made of plastic materials. In the work presented by Nuelle and co-authors, high recovery rates were

achieved (66-99%). However, the authors also reported high quantities of fibers in their blanks, probably from cross contamination due to contact with air⁹⁶.

To begin density separation, sediment and solution are mixed together, with a ratio volume/mass dependent on the density of the solution used. A NaCl solution was added to the sediment with ratio ranging (v/w, dry weight) from one to ten^{48,70}, while 250 mL of a NaI solution was added to 300 grams of wet sediment¹¹⁹. To ensure the mixing and contact of the sediment particles with the solutions for density separation, several techniques can be used: mixing with a steel spoon or glass rod, hand shaking, or stirring. In general, only several minutes were reported. The whole solution is then left to settle for periods of 1 to 48 h to ensure full separation. In order to save time, some authors performed a centrifugation technique (n=10)^{99,118}, lasting 1 to 5 min (except Haave et al.)⁷⁵, with different speeds ranging from 500 to 3900 revolutions per minute. We noted that the centrifuge tubes were made of plastic and that loss and fragmentation of MPs were reported by Haave et al.⁷⁵.

Once settling had occurred, the recovery of the supernatant fraction was seldom reported. Most studies specify that the surface layer was collected, and sometimes indicate the precise volume recuperated, but they fail to describe the techniques used. Because sediment particles can easily become re-suspended, we thus recommend that the surface fraction be collected slowly, using a glass pipette or an overflow technique^{87,109}. Either way, the tools used (beakers, tubes, Erlenmeyer flasks) need to be set up so that they slope, and must be well-rinsed after each use (MPs have a high attraction to glass surfaces). The separation step was often repeated several times consecutively, usually between 2 and 5 times. Hydrophobic solvents were used to separate MPs from the sediment matrix depending on surface properties. Crichton et al. (2017)⁶⁸ presented an oil extraction protocol using only 5 mL canola oil for 50 grams dry sediment. A high recovery rate was reported (>95%), but the protocol requires a careful cleanup step of recovered MPs, because small traces of oil can influence the subsequent optical identification. Favorably, the oil is compatible with all filter types. Organic, lipophilic stains can also be used to separate MPs from sediments depending on their surface properties, and can also be used for water samples^{131,132}. The use of Nile Red⁽⁸⁵⁾ facilitates MP counting and observation using fluorescence properties⁸⁵. Different stain types, concentrations⁸⁵ and incubation times were tested⁸⁵, with reported recovery rates ranging from 85 to 98%. However, the shortcomings of this method are that neither color nor composition can be determined after staining, as the stain also interacts with the biological matter in the sample.

III.2.4. Isolation

MP isolation aims at separating plastic particles from the environmental matrix. To do so, three techniques were usually chosen: hand sorting, sieving and filtration (Fig 2C).

Hand sorting is the most straightforward technique of the three, and was used in 6 studies of the 70 selected studies. Sample processing consisted in manually removing the target particles from dry sediment or from the surface of supernatant water⁵⁸. However, this method presents sizeable

inconveniences, being both time consuming and size-dependent. For example, Misur et al.⁸⁹ targeted only particles larger than 1 mm and Munari et al.⁹⁰ hand sorted large plastic items (large-MPs, meso- or macro-plastic waste). The authors reported a size range of plastic waste from 0.3 to 22 mm, with a predominant size range of 2 – 3 mm.

Sieving was used in 9 of the 70 studies examined. This technique permits to retain plastic particles and to eliminate the aqueous matrix as well as small particles, depending on the selected sieve cutoff. The sieves used were usually made of stainless steel, nylon and polyamide with pore sizes ranging from 30 to 315 μm . Sieving in these nine studies was performed on supernatant water resulting from density separation, but we note that it was used for both wet and dry sediment, and that several sieves could be used sequentially on a single sediment sample. Large pore size (> 1 mm for example) and sieve diameter allow to process high sample volumes. Sieves are easy to clean with filtered water and can be re-used for a batch of samples. However, the sieving technique presents two shortcomings: first, sieving is appropriate for a limited size range only (large particles in general, down to 30 μm), a constraint, which leads to a loss of size fractions of interest when studying MPs. Another drawback of the sieving technique is that MPs are not readily available for identification, so plastic particles must subsequently be manually identified.

The filtration technique combined with pumping is a rapid step that was preferred when the target size of MPs was small. Different types of filter composition were used: glass, cellulose, polycarbonate, polyester, steel, aluminum oxide, and nylon, with filter porosity varying from 0.2 to 30 μm . Filter diameter varied to a lesser extent (often 13, 25, 47 or 90 mm), which required the adaptation of the glass filtration system. We noted that filters of 0.2 μm were used in 55 of the studies on marine sediments. The two most used types of filter ($n=22$ for each) were glass fiber and cellulose filters (including nitro, nitrate and paper filters). Glass fiber filters have the advantage of being available for many identification techniques and can be pre-combusted to avoid any contamination of the sample¹³³. However, their retention size is small (0.7 to 1.5 μm among reports) which thus limits the volume of the sample being analyzed. For this reason, several filters could be used for the same sample. Cellulose filters have greater porosity than the retention size of glass fiber filters (0.3 μm to 25 μm), but they absorb the laser signal during spectrum measurements in transmittance mode (FTIR technique). Moreover, they cannot be combusted before use to avoid any contamination. Polycarbonate and aluminum oxide filters have low porosity (0.4-1.2 μm and 0.2, respectively), and, like glass filters, have the disadvantage of restricting the quantity of sample that can be analyzed. Steel filters have high porosity (20-30 μm) but are not widely available. Polyester filters have even higher porosity (250 μm), which may, nevertheless, be too high for the study of MPs, according to Graham & Thompson⁷³. A combination of different filter types was tested by Lorenz et al., who associated filters with two pore sizes (0.2 and 20 μm), which permitted a higher recovery of MPs⁸³. After filtration, the filters were removed, enclosed in glass or plastic petri dishes, and dried at room temperature, or oven-dried up to 55 °C^{64,106}, before analysis. Closed conditions are

necessary to avoid airborne contamination. Drying time varied from a few minutes to 48 h. Some studies used thick-filters and high drying temperatures¹¹¹, but this may damage the plastic polymers and is therefore not recommended.

III.2.5. Quality Assurance and Quality Control

MPs are omnipresent in the environment and quality assurance (QA) and quality control (QC) are thus necessary in MPs studies to prevent sample contamination, and identify it if it occurs. More than 70% of the studies avoided MP contamination by using clean tools as well as by respecting protocols concerning conditioning, storage and laboratory blanks. For example, laboratory equipment was washed and rinsed (one to three times) with clean water (double-distilled, demineralized or ultrapure), solvents and solutions were filtered before analysis in the closed fume hood (prewashed with ethanol 70%). Samples were protected with aluminum foil to prevent airborne contamination and/or operators were wearing cotton lab coats and gloves at all times during the analysis. Airborne contamination was identified as the main source of sample contamination. A recent review by Dehaut et al. (2019)¹³⁴ showed that the operator, the working environment, and the technical solutions used can be non-negligible sources of MP contamination¹³⁴. For the prevention of contamination, these authors suggested a QA/QC protocol which should be applied to marine sediment. We noted that some studies set a clean filter next to the sample being analyzed, and then reported the presence or absence of MP fibers on it⁶⁰. Mu et al. (2019)⁸⁹ showed that field blank concentrations were three times higher than laboratory blanks⁸⁹. Negative blanks (extraction and cleanup procedures without sediment) were also investigated and recorded 0 to 4 items per blank. A few exceptions of high blank values were reported by Frere et al. and Nuelle et al., with 19 and 39 items per blank, respectively^{57,96}. The quantity of fibers detected in blanks depended on protocol duration, laboratory conditions, solvents and technical solutions used, and according to these studies, can be subtracted from MP concentration in real samples. Solvents and solutions used also represent an important source of MPs, as shown by Vermeiren and co-authors¹⁰⁹, who reported 0, 1, 5 and 129 MPs in 200 mL of Nile Red solution, tap water, ZnCl₂ solution and deionized water, respectively. We thus recommend the filtration of solutions before use in order to avoid contamination.

Another QA/QC step consists in artificially adding MPs to sediment before applying the complete protocol. The final quantity of spiked MP enables to evaluate the procedure recovery. A third of the 70 studies reported implementing a spiking procedure using different MP types, PE, PP, PVC and PET, shape, size and color. However, recovery depended not only on MP density, but also on color and size. Using two MP types of 3 mm size for sample spiking, Tsang et al. recovered 100% of spiked PP, but only 3.3% ($\pm 5.8\%$) for PVC¹⁰⁶. Vermeiren et al. recovered more than 90% of low-density MPs (PE, PP), while dense MP (PVC, PET) recoveries were around 82-86% (MP size added range 0.30 to 0.43 mm²)¹⁰⁹. Recovery rates also depend on sediment particle size and concentration added (MP items per mass of sediment). For example, when testing six MP types (PE, PP, PVC, PET, PS and Nylon), Maes et al.

(2017) found more spiked MPs in coarse sand (77-98%) than in fine silt (65-88%). MP color was also shown to influence the recovery rate. For example, for PE of different colors with a size range of 0.1-1 mm, Stolte et al. (2015) reported high recovery rates for blue, purple and green MPs (60-100%), while recovery of yellow, orange and pink particles ranged from 0 to 40%¹⁰³. This also demonstrates that operators can introduce bias. MP spiking levels are sometime not consistent with the MP concentrations found in the field. However, spiking is an important step which permits to evaluate recovery in the overall processing protocol.

III.2.6. Recommendations for MP extraction

MP extraction is an essential step in the study of MPs in sediment. This procedure not only isolates MPs from the sediment matrix, but also helps in the identification process. Given the complexity of this procedure, we suggest that some steps must be performed prior to MP extraction. According to Dehaut et al. (2019)¹³⁴, all safeguards against airborne contamination (solvents and solutions filtered to pore size 0.45 μm , instruments rinsed three times with clean water, cotton lab coats, gloves, blank procedures in the field and laboratory) must be strictly respected at all times during analysis. Before analysis, sediment homogenization is recommended using a clean spoon. The sample can then be divided into equal parts. One aliquot use for MP analysis and another devoted for determining sediment characteristics (water, organic matter content, fraction size, and other contaminants). In this case, wet sediment is preferred in order to avoid MP degradation during sample drying. The sieving step is helpful for evaluating MP contamination at different size fractions. However, it does not seem well suited for fibers, as their retention is dependent upon their orientation during sieving. We therefore recommend that a single 5 mm mesh size sieve be employed during the elimination of large items.

Separation can be performed both before and after the digestion step. The volume of reactant required will influence the costs of analysis. Solutions for density separation should be chosen in agreement with environmental, safety, and cost considerations. Laboratories equipped with fume hoods and adequate treatment method for reagents, and lacking financial constraints, will prefer the use of NaI or ZnCl_2 to ensure the recovery of most polymers found in the environment (PE, PS, PET, PVC), while less well-equipped laboratories will prefer NaCl to recover principally PE and PS. We therefore recommend the addition of a 2:1 volume of solution to sediment mass repeated at least three times, and the retrieval of the supernatant using an overflow technique, involving the very gradual addition of extra solution until overflow occurs, followed by a thorough rinsing of the walls of the recipients three times with clean water. The literature demonstrates the necessity of a digestion step for sediment treatment, for which we recommend the use of H_2O_2 30% (m/v). The added volume is determined by the NOM content of the sediment, so this addition should be realized gradually, milliliter by milliliter, until effervescence ceases. The sample can be heated to enhance the digestion step, but the temperature should not exceed 50 $^\circ\text{C}$ to avoid MP degradation. A filtration step is also recommended to increase MP recovery. The choice

of filter type should depend both on the size range under study and also on the identification technique chosen for the following step.

III.3. Identification techniques and results reported

Materials and MP identification techniques in sediment are presented in Figure 3 (see Table 4 for details).

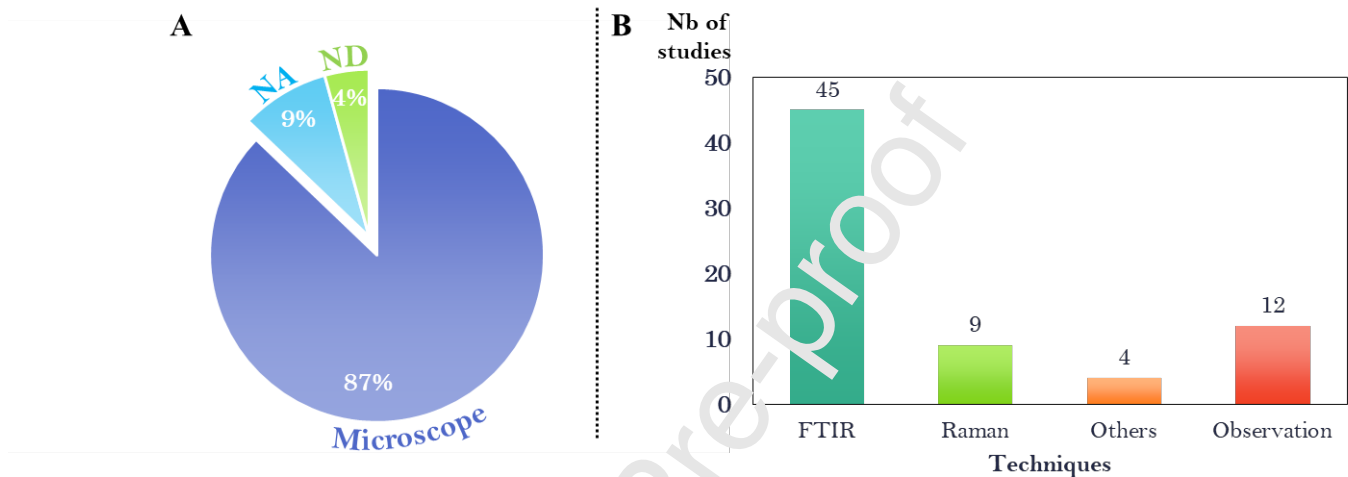


Figure 3: Techniques used for (A) visual sorting (NA=Microscope not applied, ND=technique not determined) and identification (B) of MPs in sediments, based on 70 studies.

III.3.1. Identification techniques

Ideally, all items suspected to be MPs need to be analyzed to verify their nature. This can be performed directly after visual sorting or on a filter surface. The four techniques used for MP identification in marine sediments include visual identification, Raman, FTIR microscopy and thermal analysis; all present advantages, shortcomings, and limitations, which are discussed below.

a. Visual identification

Visual identification has frequently been used for MP identification because of the tradeoff between costs and efficiency. Particles can be observed and classified based on their physical characteristics using high stereoscopic or microscopic magnification (ca. 20% (n=13) of studies). However, this technique cannot provide chemical and/or polymer composition and also involves a high risk of under or overestimation, which depends strongly on the operator⁵⁹. Hence, it shouldn't be actuated under any circumstances. The size limit for this technique depends on filter cutoff and apparatus capacity. According to two recent reviews, 100 μm is the lower size limit for visual identification^{50,135}. Scanning Electron Microscopy (SEM) can be classified as visual identification, allowing observation of particle surfaces at high resolution. This was applied in the study by Retama et al. and items were considered to be plastic when the carbon percentage measured between 60 and 72% (using energy dispersive X-ray

spectroscopy). However, the application of this technique in marine sediments is very limited, due to the expense and the high level of preparation required¹³⁶.

b. Raman spectroscopy

Raman spectroscopy is a scattering method using a laser source, often set at 532, 632 or 785 nm, which provides data about active vibrational chemical bonds which can be a fingerprint of the material/compound. Different spectral ranges can be used for MP identification (illustrated in Figure 4). The main advantage of this technique is that it is non-destructive, permitting non-contact analysis on samples of small mass¹³⁶. It allows high size resolution (down to the μm), and is thus useful for small MPs. Raman spectroscopy is, however, 10 to 100 times more time consuming than FTIR spectroscopy¹³⁷, with an analysis time depending on the selection of measurement parameters (ranging from a few seconds to several minutes per measurement). This shortcoming is exacerbated by the very small microscope aperture, which induces high sample volume for MP extraction. Another drawback of Raman spectroscopy is potential by fluorescent artifacts coming from other components, such as biological items, organic or inorganic compounds in the sample¹³⁸. Cost is another consideration in the use of Raman spectroscopy, due to the expensive instrument required. Raman micro-spectroscopy (μRaman) has been recommended strongly for the smallest MP size fraction ($<20\ \mu\text{m}$), which is not covered by the FTIR technique. Recently, some non-conventional techniques and automated identification for Raman spectroscopy have been presented and may be of growing interest in the future^{135,136,138}.

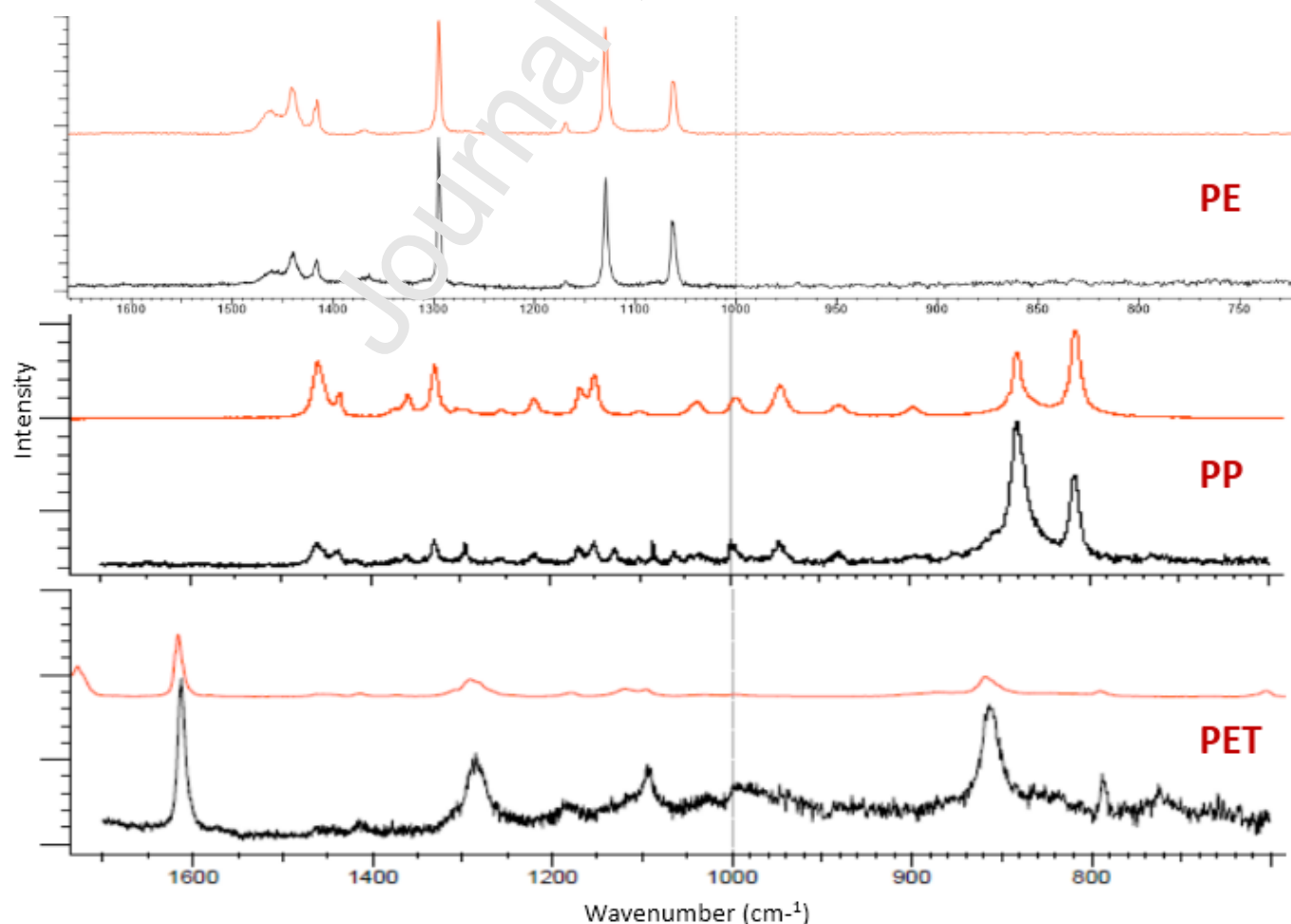


Figure 4. Examples for IRI analysis by Raman spectroscopy technique (reference spectrum in red and MP in black, measurement performed by HORIBA scientific using the laser power at 632.8 nm and treatment by KnowItALL[®] software; unpublished data).

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Table 4: Identification techniques and results obtained for studies of MPs in sediments

Visual sorting	Identification	Quantity	MPs found	References
	Chemical analysis		Qualitative (predominant)	
Stereomicroscope	FTIR-ATR/ 17 items \approx 1.08% (14/17)	141-461 items/kg dw	Fibers, fragments/ black, white/ PE, PP/ 0.1-5mm	(60)
Stereomicroscope	NA	100-900 items/kg dw	Filaments, fragments/ Black, blue/ 0.5-2mm	(61)
Stereomicroscope	Raman/ 90 items \approx 1.42% (60/90)	760 items/kg dw	Fibres, fragments/ PE, PS/ <2mm	(62)
Stereomicroscope + FlowCam	FTIR-ATR/ 177 items (31/177) + μ FTIR transmission	42-6595 items/kg dw	Chlorinated polyethylene, polyamide/ < 25 μ m (80%)	(63)
Stereomicroscope	NA	29 items/sample	Filaments, fragments/ Clear, red/ 0.063-1mm	(64)
Dissecting microscope	FTIR 116 items (105/116)	730-2300 items/kg dw	Fibers/ Blue, black/ PTFE, PE	(65)
Microscope	FTIR transmission	32 items/sample	Fragments/ PVC, polyester/ <1mm	(42)
Stereomicroscope	NA	6 ³ - 106 ³ items/kg	Filaments/ Black, blue	(43)
Nd	FTIR	> 3% by weight	Fragments/ PE, PP	(66)
Dissecting microscope	FTIR-ATR/ 380 items \approx 21.1%	9 ² -298 items/kg ww	Fibers, films/ PE, PET/ 0.3-5mm	(44)
Binocular microscope	FTIR reflection	49 - 391 items/kg dw	Fibers, granules/ PP, nylon/ 0.038-1mm	(56)
Microscope	FTIR	29 - 144 items/kg dw	Fibers, fragments/ Blue, green/ PE/ >0.1mm	(67)
Microscope	FTIR	4.15 items/sample	Fibers, fragments/ dark, blue/ 0.5-1mm	(68)
Stereomicroscope	TD-PYR-GC/MS (15/32)	1.3 - 2.3 items/kg dw	Fragments/ PP, PE/ >0.1mm	(69)
Microscope	μ FTIR-ATR/ 85 items \approx 14%	101 - 431 items/kg dw	Foam, fragments/ CP, PS/ 0.1-5mm	(70)
Stereomicroscope	Raman (30/229)	0.97 \pm 2.08 items/kg dw	PE, PP/ 0.335-1mm	(57)
Stereomicroscope	TD-PYR-GC/MS	5 items/sample	PE, PP, PS/ 0.01-0.35mm	(71)
Stereomicroscope	μ FTIR reflection	0-53 items/kg dw	Fibers, fragments/ transparent, red/ PEST/ 0.1-4mm	(72)
Dissecting microscope	NA	105-214 items/L	Filament/ transparent, blue/ <0.25mm	(73)
Microscope	NA	45 - 1069 items/kg dw	Filament, fragments/ black, white/ 0.5-1mm	(74)
Stereomicroscope + FlowCam	FTIR-ATR/ 429 items (188/429) + FTIR imaging	12-20 items/g dw	PUR/ <0.1mm	(75)

Microscope	Raman	48±55 items/kg dw	Fibers/ blue	(77)
Stereomicroscope	μRaman/ 25% (94%)	2433±2000 items/kg dw	Fragments, pellets/ blue/ PP, PE/ >1mm	(78)
Microscope	FTIR	100-3600 items/kg dw	Spheres, fibres/ >0.3mm	(79)
Stereomicroscope	μRaman	520-1860 items/kg dw	Transparent, white/ PP, PE/ <1mm	(80)
Dissecting microscope	NA	<49600 items/kg dw	Granule, fibers/ <0.1mm	(81)
Dissecting microscope	NA	4110 items/L	Filament/ 0.038-0.25mm	(82)
Stereomicroscope + FlowCam	FTIR-ATR + FTIR imaging	3-1189 items/kg dw	PE, PP/ <0.5mm	(83)
Stereomicroscope	Raman/ 221 items (129/221)	72-1512 items/kg dw	Fibers, film/ Sh, black / polyester, PP / <1mm	(84)
NA	FTIR – Fluorescent		Fragments, fibers/ PE, PP	(85)
Binocular microscope	μFTIR transmission	185.1 items/m ²	Fragments/ PE, polyester/ 2-5mm	(86)
Dissecting microscope	NA	2-8 items/g	Fibers	(87)
Nd	FTIR-ATR	100-1000 items/kg dw	Fragments, fibers/ white, brown/ PE, PP/ 0.315-1mm	(88)
Dissecting microscope	FTIR-ATR	0.58 items/ m ²	Filament, fragments/ Nylon, PE/ 1-5mm	(88)
NA	μFTIR	0.8 items/kg dw	Fiber, film/ white, black/ PP, PET/ 0.1-0.2mm	(89)
Dissecting microscope	FTIR-ATR/ 20 items ≈ 1.2%	0.08 items/m ²	Fibers, film/ Nylon, SBS/ 2-3mm	(90)
Stereomicroscope	FTIR/ 81 items ≈ 1.9%	2-1258 items/kg dw	Fibers, film/ PET, PE	(91)
Stereomicroscope	FTIR/ 68 items ≈ 22% (60/68)	0-125 items/kg dw	Fibers, film/ PET, PE/ 1-4.7mm	(92)
Stereomicroscope	FTIR 209 items	19.5-34.5 items/kg dw	Fibers, fragments/ black, blue/ PE, Nylon / 0.01-0.3mm	(93)
Dissecting microscope	NA	700-3300 items/m ²	Fibers, fragments/ Blue, black/ 0.065-5mm	(94)
NA	FTIR reflection (5 x 3mm ²)	0-16 items/kg dw	PE, PS	(11)
Microscope	FTIR-ATR	12-63 items/kg dw	Fibers, film/ PE, PP, PVC/ <0.04mm	(95)
Stereomicroscope	TD-PYR-GC/MS		Fibers/ Blue, red/ PP, PET, PVC/ 0.5-1mm	(96)
Dissecting microscope	μFTIR transmission/ 65 items ≈ 11.4%	121±9 items/kg dw	Fibers, fragments/ Transparent, blue/ Rayon, Polyester/ <1mm	(97)
NA	μFTIR reflection	67±76 items/kg dw	Fragments, fibers/ PP, PE/ grey, white/ 0.1-0.25mm	(98)
Microscope	FTIR transmission	81 mg/kg dw	Fragments/ Styrofoam, Nylon/ Transparent	(99)
Stereomicroscope	SEM	0-69 items/30g dw	Fibers/ white, black/ Polyester, PE	(100)
Microscope	Raman	15/44 locations	Filament, fragments/ blue, white/ PP, PE	(101)

Binocular microscope	NA	0-18 items/kg dw	Fibers/ Transparent	(103)
Dissecting microscope	NA	0-18 items/kg dw	Fibers/ Transparent	(103)
Microscope	μFTIR	76-333 items/kg ww	Fibers, granules/ black, transparent/ PP, PE	(104)
Microscope	FTIR transmission	86 items/kg ww	Fibers, fragments/ 9 natures/ brightly colored	(105)
Stereo microscope	FTIR-ATR (110/240)	47-279 items/kg ww	Fragments, pellets/ transparent, white/ PP, PE/ 0.01-4.7mm	(106)
Microscope	NA	7-20 items/kg dw	Fibers, granule	(107)
Microscope	Raman	1-23 items/kg dw	0.03-1mm	(108)
Binocular microscope	FTIR – Fluorescent (110/120)	111-8128 particles/L ww	PE, PP/>0.125mm	(109)
NA	μFTIR reflection (12 x 4.5mm ² ≈ 5.6% area)	672-2173 items/kg dw	Fragments, fibers/ PE, PP/ 0.03-0.5mm	(110)
Stereo microscope	μFTIR/ 65 items	32947 items/kg dw	Fragments, fibers/ PE, PP/ 0.02-0.3mm	(58)
Stereo microscope	FTIR/ 200 items	560-4200 items/kg dw	Fibers, granules/ Red, transparent/ PP, Polyester/ 0.05-1mm	(111)
Stereo microscope	FTIR/ 679 items ≈ 33.4% (622/679)	225-500 items/kg dw	Fibers, fragments/ rayon, PP/ 0.032-0.5mm	(112)
Nd	FTIR-ATR	5-117 items/m ²	hard, films/ PP, PE/ 0.2-1mm	(113)
Stereo microscope	NA	2.4-4.7 items/g tw	Fibers, sheet/ transparent, black/ <1mm	(49)
Binocular microscope	FTIR transmission	1-440 items/50mL	Fibers/ blue, black/ Polyester/ 2-3mm	(114)
Microscope	μFTIR transmission (51/366)	30-240 items/kg dw	Fibers, fragments/ transparent, blue/ PE, PET/ 0.06-1mm	(115)
Stereo microscope	μFTIR transmission (214/228)	140-1873 items/kg dw	Fibers, fragments/ rayon, PP/ 0.035-1.5mm	(116)
Microscope	μFTIR transmission/ 178 items ≈ 16.2% (173/107)	72-172 items/kg dw	Fibers, fragments/ rayon, PE/ 0.06-1mm	(117)
NA	μFTIR-ATR	7-25 items/kg dw	Fibers, fragments/ black, blue/ PET, PP/ <4mm	(118)
Stereo microscope	μFTIR transmission/ 60 items ≈ 18.5% (24/60)	37±43 items/kg dw	Fibers, film/ transparent, black/ PP, PE/ <0.5mm	(119)
Stereo microscope	NA	34±10 items/kg dw	Fragments, films/ >0.175mm	(120)

Nd (not determined), N.A (not available),

FTIR (Fourier transform infrared spectroscopy), ATR (attenuated total reflection), PYR-GC/MS (pyrolysis gas chromatography-mass spectrometry); this column has number items sorted with percentages of total items suspected to be Microplastic; in parentheses are presented the number of identified items out of total items.
dw (dry weight),

PE (Polyethylene), PP (Polypropylene), PS (Polystyrene), PTFE (Polytetrafluoroethylene), PVC (Polyvinyl Chloride), CP (Cellophane), PEST (Polyester), PUR (Polyurethane), SBS (Polystyrene butadiene styrene), PET (Polyethylene terephthalate) and PMMA (Polymethyl methacrylate); this column presents MPs qualitatively with respect to shape, color, nature and size.

c. FTIR spectroscopy

FTIR spectroscopy, like Raman, is a non-destructive technique. It is automated and is based on the two principles of reflectance and transmission with a short analysis time. FTIR is quite easy to maintain and is therefore the technique of choice for the study of MPs, and indeed represented 77% of all techniques used (five times more than Raman spectroscopy). It is a vibrational technique with an IR source which produces information on IR absorption that is connected to the nature of chemical bonds such as C–H, C=H and C=O are very easily detected by FTIR.¹³⁷ It has three working modes, and is thus more selective than Raman spectroscopy. When compared to Raman spectroscopy, FTIR provides strong intensities on some chemical groups such as –OH and C=O, which is of importance for MP degradation studies (e.g. photo-, bio-oxidation)¹³⁸. However, the resolution size drops to only 10-20 μm in the FTIR technique. As was seen for Raman spectroscopy, expensive instrumentation is a limitation of this technique (especially for μFTIR). An IR beam passes through the particle being measured, the signal obtained after total penetration of the particle and filter (named the transmission mode) is reflected onto the particle's surface in the reflectance mode. The transmission working mode provides better information than which other one. However, transmission mode selected the filter composition and problematic on the thickness of particle. In reflectance, the ATR-FTIR working mode is in direct contact with the particle (on the interface of the crystal), which possibly eliminates the influence of the environment. However, contact-analysis is one drawback of this mode, because the crystal interface may affect another particle when measured directly on the filter. On the other hand, single measurements are possible but require the sorting of particles (hand picking in general, with limitations of particle size).

FTIR-imaging has been widely used and large databases are now available¹³⁵. An MCT detector (mercury cadmium telluride) was used in early study¹¹⁰, despite being size limited (150-200 μm) and very time consuming¹³⁶. An FPA detector (Focal Plane Array) was then developed for MP studies in the environment¹³³. Size constraints for the FPA detector are as small as 11 μm , but the method is still time consuming and generates very large amounts of data⁸³. For example, Bergmann et al. analyzed 166 mm^2 of filter area, and obtained results with 1.36 million spectra over a period of 13 hours⁶³. Other shortcomings of FTIR-imaging are the requirements for a high purification step and the expense of the instrument (which exceeds that of the μFTIR system).

d. Thermal analysis

Thermal analysis consists of the pyrolysis of particles at high temperature without oxygen, followed by GC-MS detection of the products, which can provide the peaks specific to the polymer composition. Such techniques were used in 3 studies on MP measurements in marine sediment, and enable the simultaneous detection of organic plastic additives (OPAs) such as phthalates (DEHP, DBP, DEP, DIBP and DMP)^{69,71,96}, which cannot be detected using vibrational techniques (Raman and FTIR). The comparison of pyrogram between MP standard and particles sampled permit to identify the particle composition and plastic additives in a single measurement⁷¹. For example, Fries et al. (2013)⁷¹ identified

seven OFAs in eight MP collected in sediment from Nordemney (German East). These compounds were found randomly distributed in MP analyzed^{69,71}. However, there are certain limitations to the application of this technique. For example, the destructive aspect of the method and the lack of information related to MP size and counting. Furthermore, this method is better adapted to single selected particle analysis (a few μg in the mass), and remains time consuming when samples are analyzed thoroughly. For example, an item analyzed by Raman or FTIR requires a few seconds to a few minutes (depending on acquisition parameters), while a pyrogram requires around 30 minutes. The limited application range in terms of size ($>100 \mu\text{m}$, operator dependent) is an additional drawback of this technique. Given the high level of attention currently paid to plastic additives, thermal analysis remains the ideal technique to complement FTIR or Raman spectroscopy.

III.3.2. Results reported

a. Quantitative results

Depending on the sampling technique and the sample preparation step chosen, MP concentrations in sediment are often expressed as items per mass (g, kg), per surface (m^2) or per volume (mL, L). They are convertible if enough sample information is available. Highly variable results have been reported so far, ranging from 0 to 50.000 MPs per kg of sediment (dry weight), 30 to 8.000 MPs per L, and 0 to 3.300 MPs per m^2 . This variation results from the multitude of locations studied as well as from the different protocols and identification techniques used. The highest quantities were reported on German beaches in terms of mass concentration (East Frisian Island, North Sea), on the Japanese coast for volume concentration and on the South African coast as far as surface concentration is concerned^{81,94,109}. Conversely, the lowest values were found in the Southern Baltic Sea (MPs by mass), in the Southwestern Indian Ocean (MPs by sediment volume) and in the Adriatic Sea (MPs by sediment surface)^{72,88,114}. The highest values were found in beach and coastal sediments while the lowest values were reported in open ocean sediments.

b. Qualitative results

Qualitative results play an important role in MP studies as the crucial information they reveal can provide hints as to potential sources. The four characteristics most used for MP reports are: nature (polymer chemical composition and density), form, size and color. To establish MP nature, a particle is considered to be made of plastic when its chemical composition corresponds to a referenced plastic material. The literature indicates that the major MPs found in sediments comprise four polymer types, including PE (toys, milk bottles), PP (bags), PS (food packaging) and PET (water bottles). This is consistent with available figures for worldwide production and utilization³. While MP nature is consistent between studies (that is not influenced by protocols or operators), other characteristics of MPs (size, form, and color) are highly study-dependent. Nevertheless, size, color and shape are useful as descriptive parameters recommended by the European MSFD technical subgroup on Marine Litter¹⁴⁰. MP size can be determined from image analyses or directly taken from microscopic observation. Previous studies have

shown that small (1 μm to 1 mm) and large MP (1 mm to 5 mm) are the two most common MP size ranges detected, yet it is noteworthy that although some MP studies include plastic items inferior to 1 mm in size, <5 mm is the most widely accepted size range in other studies^{42,56}. Indeed, agreement on a lower size limit for MPs has failed to reach a consensus, mainly due to the specificities of the different protocols applied. For example, by sieving at 38 μm , Claessens et al. reported a single MP size range of 0.038 to 1 mm⁵⁶. Other studies endorsed sizes of MP >100 μm using hand picking and >300 μm for sieving⁷⁰⁻⁷¹. MP size class is also divided into sub-classes in agreement with i) sieve pore size: <63 μm ; 63 μm to 1 mm; 1.1 to 2 mm; 2.1 to 4 mm and 4.1 to 5 mm, ii) the identification procedure: 11 to 25 μm ; <150 μm ; <500 μm and >500 μm , or iii) the results obtained: 20 to 50 μm , 51 to 100 μm and >100 μm ^{63,64,98}. As far as MP shape categories are concerned, the three most reported categories are fibers, filaments and fragments. MP shape can be observed and recorded with the naked eye or with a microscope. Other forms are listed in Table 4, and include granules, foams, films, pellets, and spheres, all of which may provide consistent information as to MP sources. Most contamination occurring during sample processing originates from fibers, due to their omnipresence in both outdoor and indoor atmospheres. Some studies therefore excluded fibers from their reports^{42,66}. Fibers are also difficult to identify when they are too fine. For these reasons we highly recommend the shape ranking proposed by Galgani et al.¹⁴⁰.

Regarding MP color, 12 different categories are proposed by Galgani et al.¹⁴⁰. MP color is recorded by direct observation by the operator of the experiment. According to several of the studies, many colors were reported for MPs found in marine sediments, including black, white, red, blue, transparent and brown. The designation of color must, however, be treated with caution. For example, an apparently transparent MP may (i) have undergone long environmental weathering leading to loss of color, (ii) have lost its color during sample treatment (e.g., during organic matter digestion), (iii) appear transparent due to the light density during measurement, or (iv) be intrinsically transparent⁶⁵.

III.3.3. Recommendation for MP identification and results report

To date, the identification of all MP extracted from marine sediment is not yet feasible due to time of analysis and/or the limitations of the techniques used. Studies reviewed here were often performed only on items suspected to be MPs (using microscopic observation). The ratio (items selected/items extracted) and identification are presented in Table 4: 25 studies treated this issue. Firstly, it could be shown that small ratio sorted (1 to 33% of total) then verified as MP via spectrum measure. This seems reasonable because many particles with different characteristics remain on the sieve/filter. For this reason, hand sorting of MPs is very time consuming or even impossible for the smallest items. Once an item is isolated, it is possible to classify it as being a MP, or to rule it out after verification using various identification techniques. The values (accepted items / total items) are presented in parentheses in the chemical analysis column of Table 4. Positively, high ratio of items selected are verified as MP among these reports which up to 92%^{109,112}. An automatic MP identification that would exclude these biases would be optimal for future work.

For accurate MP identification, we suggest that the composition of at least 10% of items (chosen randomly) be verified. Successful rate (items accepted/items total) will be used for whole items observed. A combination of techniques would permit to identify all items and with more consistency. This suggests that three fractions of MP size should be measured separately: large sized items ($>500\ \mu\text{m}$) using FTIR-ATR, medium sized pieces (ranging from 20 to $500\ \mu\text{m}$) *via* μFTIR (reflectance or transmittance), and small size particles ($<20\ \mu\text{m}$) using Raman spectroscopy. Regarding instrument cost, Raman spectroscopy and μFTIR may not be within the means of all laboratories but difficulties in accessing these instruments could be overcome by cooperation between institutions. For organic plastic additives in MP, thermal analysis is recommended. On the other hand, chemical extraction has been well developed in recent years for these compounds¹⁴¹⁻¹⁴³.

Concentration report can be calculated by number of MPs on dry mass, although we recommend a protocol on wet sediment but convertible with water content. When results are calculated by volume or area, full sampling information should be provided to ensure reliability. As the most-used means of MP identification, the categories proposed by Galgani et al. are strongly recommended for use and reporting.

IV. Challenges of Nanoplastics

Although studies on MP size fractions will vary due to the various methodologies being used as presented above, the attention paid to the smallest fraction at the nanoscale (nanoplastics, NPs, 1 to 100 nm)¹⁴⁴ has been growing since 2017. In theory, a $50\ \mu\text{m}$ MP (the size most commonly found in the environment) could fragment into up to 125 trillion NPs of 1 nm size, which would have a much bigger active surface area. These particles also have a higher accumulation capacity and a higher toxicity, possibility due to more efficient trophic transfer and potential cell penetration. Just like MPs in the environment, NPs have two distinct sources. While primary NPs originate from personal care products, the secondary source comes from the fragmentation of plastic waste due to environmental conditions¹⁴⁵. Sharing the same workflow as MP analysis, methods used for the NP size fraction have some principal steps such as sample preparation, filtration and identification. To date, only few studies have reported the presence of NPs in seawater and snow samples and analysis is still limited to a few polymer types^{146,147}. The sample preparation step requires a combination of multiple sub-steps in order to purify the sample. For environmental samples, a digestion step is necessary due to the presence of natural organic matter. Other non-plastic materials must be removed as good as possible. Furthermore, NP mass concentrations in the environment are often very low and therefore require a high pre-concentration rate of the sample¹⁴⁴. Once the sample is purified, particles bigger than $1\ \mu\text{m}$ can be removed using a filtration technique, while the smaller fraction is used for NP analysis. Some techniques such as ultrafiltration, ultracentrifugation, evaporation of solvent or dialysis may help to concentrate the sample^{148,149}. When studying MP size fractions, particles are identifiable by measuring the residue on the sieve or filter surface using spectroscopy. However, this method is not yet applicable for NP size fractions. Several techniques can be

used for NP separation (field flow fractionation, chromatography, and electrophoresis) and NP characterization (light scattering, electron microscopy)¹⁴⁹. The identification of NPs is more difficult, requiring a combination of analytical methods, and is therefore more expensive¹³⁵. Direct identification of large NPs (> 450 nm) could be achieved by using HR SEM (High Resolution SEM) combined with Raman or imaging mass spectroscopy TOF/SIMS (Time of flight secondary ion mass spectrometry)^{150,151}. However, this approach needs to be further developed. On the other hand, a thermal analytical method coupled with mass spectrometry seems more utilizable for NP identification. Thermal treatment (Py – pyrolysis or TED – thermoextraction and desorption) allows to have low molecular weight from macromolecules. These molecules are then separated and analyzed using GC-MS to identify the polymer composition¹⁵². The recently developed Raman tweezers technique allows to identify NPs down to 50 nm in seawater samples¹⁵³. The study of NPs in marine sediments has not yet been reported but constitutes an important research topic for the future.

V. Conclusion

Different protocols are used for the evaluation of MP contamination in marine sediments. It is thus difficult to compare the reported results and to draw up a reliable protocol for future studies. With the aim of obtaining comparable results, our recommendations are resumed in Figure 5.

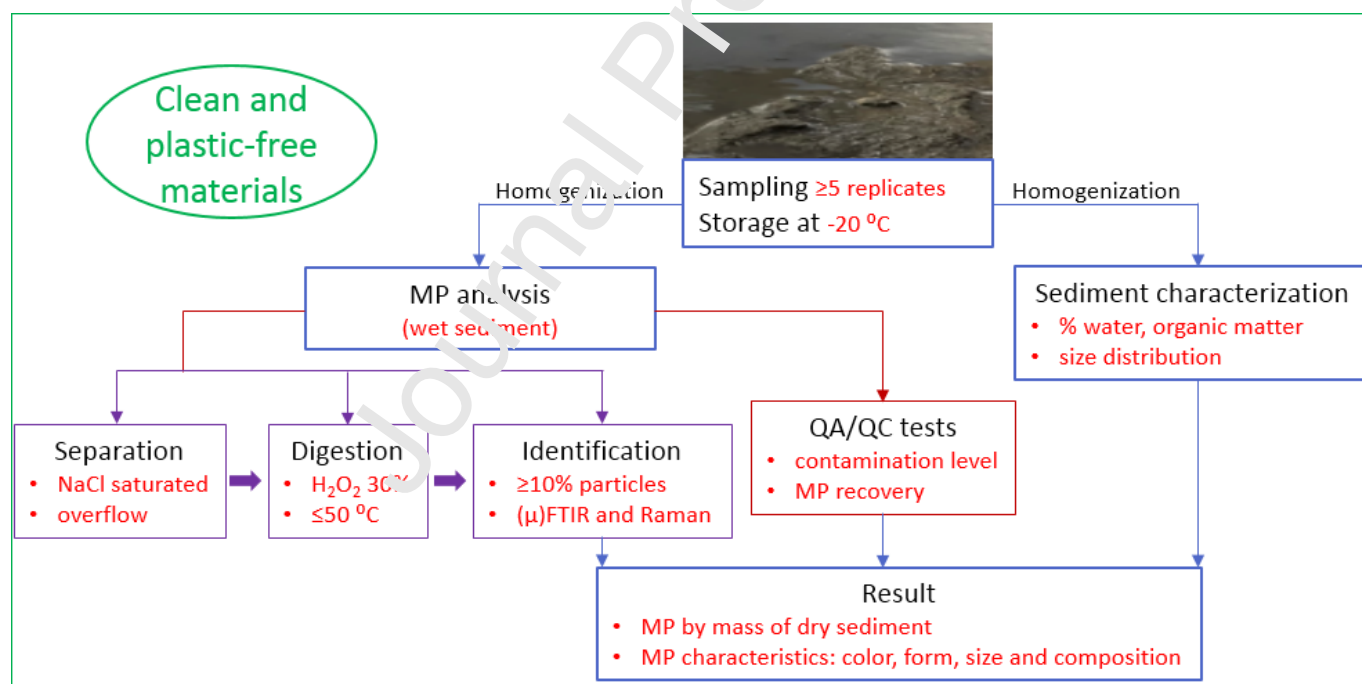


Figure 5: Recommendation for a reliable workflow of MP analysis in marine sediment

Taking into account aspects dealing with cost and ecology, we recommend the use of NaCl solution for the separation step. Although there are many denser solutions available for use such as $ZnCl_2$, $CaCl_2$, NaI, each one has shortcomings, including viscosity, toxicity or expense when compared to a NaCl solution. A digestion step using an H_2O_2 solution should be applied for organic matter elimination. This solution is more readily available than enzymatic solutions, and has less influence on MP degradation

than operating with alkaline and acid solutions. The nature of MPs can be well identified by spectroscopy. Vibrational spectroscopies (FTIR and Raman) have been shown to be the techniques of choice. We further suggest the measurement of sediment characteristics (size distribution, water and organic matter content) in parallel with those used for MP analysis. The QA/QC (blanks analysis, spiked samples, working conditions) must always be respected to prevent sample contamination, and enable the evaluation of MP recovery depending on the protocol used. The use of plastic-free apparatus during sample processing is a necessity for the prevention of a large part of sample contamination. Automatic identification (involving neither the naked eye nor microscope observation) is recommended to avoid operator bias (*e.g.*, μ FTIR). The very recent technique of LDIR (Laser Direct Infra-Red) may also be a valuable solution but it has not been applied to marine sediments yet. Lastly, the occurrence of NPs in marine sediments is a new analytical challenge that will need to be tackled in the coming years.

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Declaration of competing interest

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

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Highlights

- MPs in marine sediments have been published in at least 70 articles, at a total of 813 locations on all continents
- Areas studied are mainly in coastal environments, and the number of locations examined per study ranges from 1 to 72.
- We recommend the use of a NaCl solution for the separation step.
- A digestion step using an H₂O₂ solution and automatic identification are recommended

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