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A critical review of the novel analytical methods for the determination of microplastics in sand and sediment samples

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ABSTRACT

Microplastics (MPs) form the most investigated plastic category since their size (1 μm- 5 mm) enables them to accumulate in various environmental compartments and to be ingested by biota. Beach sand and sediment can be indicators of the MP contamination levels of the coastal and marine ecosystem and, thus, they are widely analyzed. With the increasing number of publications in recent years, there is a need for constant updates on the variety of extraction and analysis procedures developed. Thus, this review aims to evaluate the sample preparation techniques for MPs and provide a critical discussion on their determination in sand and sediment based on studies published in the last 5 years. We also report the conditions imposed by the MPs identification and quantification techniques on sample preparation and MPs isolation as well as the materials used in the procedures. Finally, we address the expectations and new challenges related to instrumental innovations.

1. Introduction

Plastics production has increased exponentially during the last decades and their use is an indispensable part of the industrial and commercial activity. They are cost-effective and biodegradation resistant, qualities that promote their wide presence in human daily life [1]. There are thousands of types of different plastic polymers, each with its own composition and characteristics with the most common being polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinylchloride (PVC) and polyethylene terephthalate (PET) [2,3] (illustrated in Fig. 1). Almost 80% of plastic is not properly recycled and is, therefore, released as waste in the environment [2]. Even some coined as biodegradable and/or compostable plastics, which are intended to replace conventional ones, still contain polymers that cannot be fully biodegraded under environmental conditions [4].

Plastic debris is categorized according to its size as macroplastics (>5 mm), microplastics (MPs, <5 mm) and nanoplastics (NPs, <1 μm) [2]. The presence of plastic debris is widely recognized as a significant environmental issue and its potential implications for human health have garnered considerable interest from the scientific community, resulting in a substantial number of studies being published annually [2]. The term microplastic was firstly introduced in 2004 by Thompson et al. [4] and since then these particles have been extensively analyzed due to the hazardous effects they can have on living organisms [2,3]. MPs can accumulate in various environmental matrices including water, sediment, soil, sand, and algae, due to their small size. Additionally, they are easily ingested by biota as they can be mistaken for food [1,2]. Another aspect that enhances their toxicity and increasingly attracts the scientific interest is their potential role as vectors for bacteria, toxic inorganic trace elements, persistent organic pollutants (POPs) as polycyclic aromatic hydrocarbons (PAHs) [5], and contaminants of emerging concern (CECs) such as pesticides, pharmaceuticals and personal care products (PPCPs) or perfluoroalkyl substances (PFASs) [6,7].

Coastal environments are highly affected by plastic debris [8]. Anthropogenic activity, mainly touristic and industrial, is responsible for this contamination in beach and marine sediments [6,9]. The pollution of sand and marine sediments around the world, ranging from large plastics (macroplastics) to MPs and NPs, has been extensively documented. These matrices serve as indicators of MP pollution along the coastlines. The profuse proliferation of scientific publications in this specific field poses significant challenges in maintaining up-to-date knowledge on the employed analytical tools and the quality of the results they yield. The study of MPs extraction methods developed in recent years together with the advances in their determination will provide an overview of the challenges and opportunities for future research in this field.

Plastic debris enters the coastal environment mainly by land [6]. The

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Abbreviations

^{1}H NMR	Proton nuclear magnetic resonance
AIO	Air-induced overflow
ATR	Attenuated total-reflectance
DAD	Diode Array
DAPI	4′,6-diamidino-2-phenylindole
DART MS	Direct analysis in real time mass spectrometry
DCM	Dichloromethane
EDS	Energy Dispersive Spectroscopy
FESEM-EDS	Field emission scanning electron microscopy with energy dispersive X-ray spectroscopy
FITC	Fluorescein isothiocyanate
FLD	Fluorescence Detector
GF	Glass fiber filter
GPC	Gel Permeation Chromatography
HCl	Hydrochloric acid
HDM	Hot-stage microscopy
HPLC	High Pressure Liquid Chromatography
HSI-NIR	Near-infrared hyperspectral imaging
LC-MS	Liquid chromatography coupled with mass spectrometry
LDPEox	Polyolefins
LMT	Lithium Metatungstate Solution
LOD	Limit of detection
LOQ	Limit of quantification
MAE	Microwave assisted extraction
MeOH	Methanol
MPs	Microplastics
NIR	Near-infrared
NOAA	National Ocean and Atmospheric Administration
NPs	Nanoplastics
PA-6	Polyamide-6
PAHs	Polycyclic aromatic hydrocarbons
PE	Polyethylene
PET	Polyethylene terephthalate
PISA	Polymer identification and specific analysis
POPs	Persistent organic pollutants
PP	Polypropylene
PPCPs	Pharmaceuticals and personal care products
PS	Polystyrene
PVC	Polyvinylchloride
Py-GC–MS	Pyrolysis- Gas Chromatography–Mass Spectrometry
RP	Reversed phase
SD	Standard deviation
SEM	Scanning electron microscopy
SEM-EDX	Scanning electron microscopy with energy dispersive X-ray spectroscopy
SIMCA	Soft Independent Modelling of Class Analogy
SMI	Sediment Microplastic Isolation
UV	Ultraviolet
VIS	visible
WWTPs	Wastewater Treatment Plants
XPS	X-ray photoelectron spectroscopy
μ-FTIR	micro- Fourier-Transform Infrared
μ-Raman	micro- Raman spectroscopy

MPs pollution in freshwater environments has not been as extensively studied as in the coastal environments due to the false perception that wastewater treatment plants (WWTPs) can effectively eliminate all plastic pollutants [10]. Direct sources of MPs release into freshwater systems include WWTPs, degradation of larger plastics in rivers and lakes, and erosion of MP-contaminated soil with subsequent surface runoff transport [11]. Soil systems are more affected by plastic pollution than the aquatic environment since they are considered sinks for MPs [12,13]. The extraction of MPs from soil is like the one used for beach sand and sediment that will be further analyzed, but some differences are observed mainly in the digestion step of the protocol.

Numerous reviews have already been published on the analysis of MPs in various environmental matrices, and in many cases, these may include sand and sediments of the beaches [14–17]. However, in these cases, the specific aspects that affect these matrices are not explained in depth when discussing the topic in a more global sense. Some other reviews report the determination of the MP pollution in beach sand and sediments but they discuss specific geographic regions such as the coast of Latin America and the Caribbean, the Asian coast and the Mediterranean region [1,3,6]. Moreover, these are focussed on the quantification results, analytical standards available and outlined guidelines for MP analysis and not on the analytical methods used. Other review articles include studies about the migration and the behaviour of MPs and MP additives [18,19] and, others analyze the impact of the methods used for the extraction, sometimes even focusing on one specific protocol such as density separation and the use of different salts [20] or the determination and the degradation of MPs in the environment in order to establish whether these methods are environment friendly or not [21,22]. However, since 2017, a review that only focuses on the latest advances in the analysis of MPs in sand and sediment (combining studies around the globe) and that outlines how to proceed with the particularities of the specific matrix has not been published.

In this review, we focus on a critical discussion of the analytical methods for determining MPs in beach sand and sediment. We include the most recent advances in the methodologies used for the separation and the extraction of MPs, as well as the novel analytical tools that are employed for their characterization and quantification. Furthermore, the requirements that the determination technique imposes on sample preparation, which have been little taken into account, are considered here. This review offers cutting-edge information and a better understanding of the current methodologies (last 5 years) to determine MPs in two matrices that could indicate the actual contamination levels of coastal and marine ecosystems, aiming towards a harmonization of protocols and results reporting.

2. Extraction of MPs from sand and sediment samples

The sample pre-treatment and extraction protocol to identify MPs in environmental samples is selected according to the matrix type and the analytical instrumentation for the final determination. The type of matrix plays a crucial role. The two main categories of sediments are the sandy sediments (main component is sand) and the bed sediments (mostly fluvial sediments). Their composition is completely different, with sandy sediments containing bigger particles and low organic matter levels. The most common constituent of sand is silica (silicon dioxide or SiO_2), usually in the form of quartz (in general chemically inert) followed by calcium carbonate ($CaCO_3$) that can become major component in biogenic samples (e.g. coral sands). On the other hand, bed sediments are formed by different size particles (clay: <2 μm of particle diameters, silt: between 2 and 50 μm, and sand: between 50 μm and 2 mm) and a large amount of organic matter, being also highly reactive, usually with negative charges, which allow them to absorb cations [23]. Additionally, they have high specific surface area (m^2/g), which increases their potential to absorb organic material and particles, such as MPs [24].

In this section, the pre-treatment, density separation, digestion and other extraction protocols reported during the last 5 years are discussed. Details on the methods for the extraction of MPs from sand and sediment samples can be found in Table 1 and Table 2, respectively. It should be

noted that most of the methods use a combination of density separation of MPs and then, once isolated on a filter, digestion of the organic matter using mostly H_2O_2 and the Fenton reagent (H_2O_2+Fe^{2+}). The oxidation of the organic matter probably works better after separation, since the optimal catalytic effect of Fe^{2+} is at pH < 3 but at this pH the carbonates contained in sand are highly reactive and transform abruptly to CO_2.

2.1. Sample pre-treatment

The pre-treatment of the sand and sediment samples mostly includes drying and sieving to obtain fractions of different sizes before further extraction [9,25,29,33,34]. Most of the studies perform the sampling in the strandline where the tide ends and so, the sample is generally humid and requires drying before it can be sieved [25,41,48]. Although, in few cases the sand is already dry and so, this step is omitted [32,33], most studies include the drying step. This procedure is performed in the laboratory at room temperature [8,29,63], or heating in an oven at temperatures ranging from 40 to 104°C [26,28,41,54]. As far as sediments are concerned, drying is always carried out, since the sample is wet, and it could not be sieved easily otherwise. Freeze-drying [36],

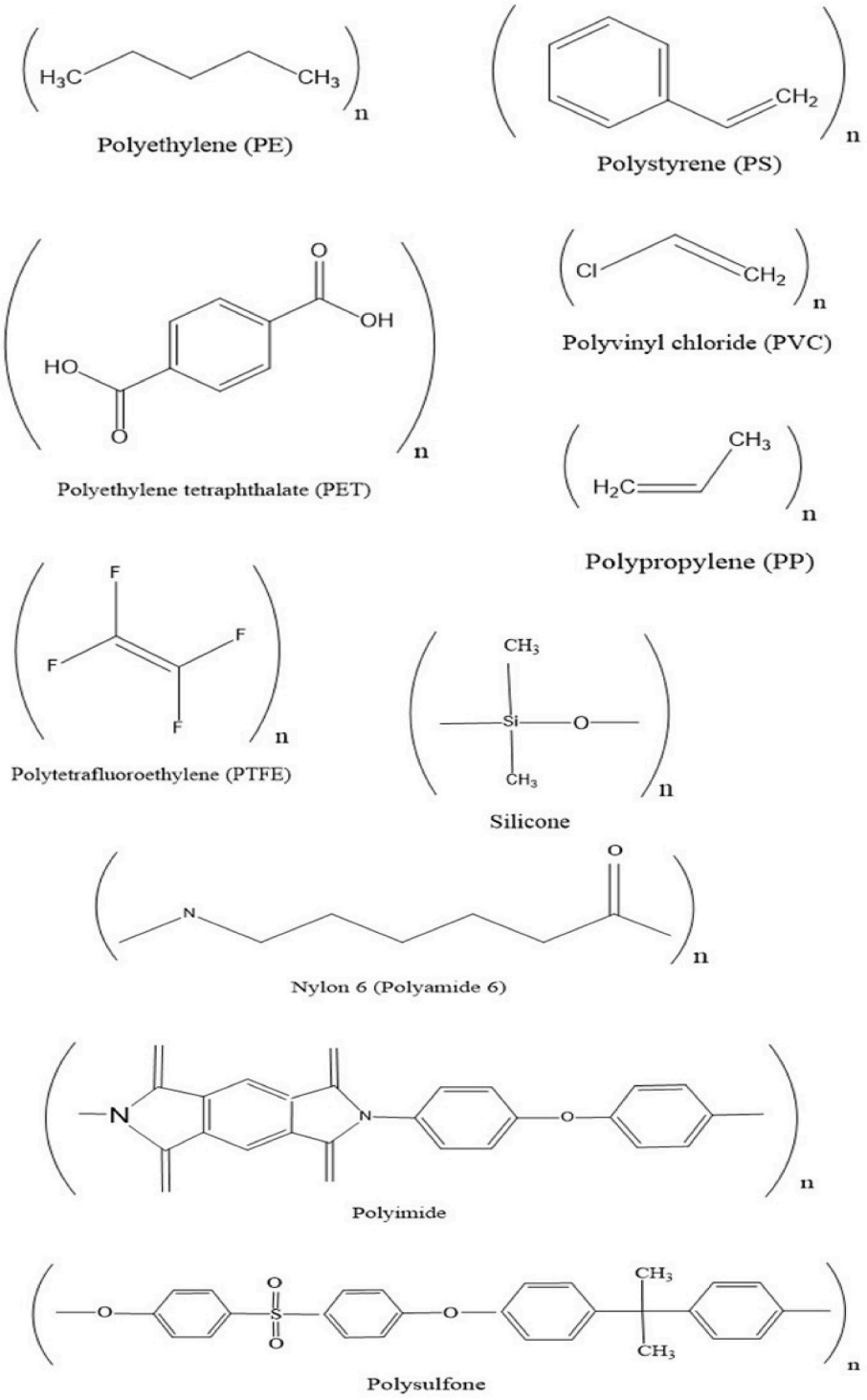

Fig. 1. Examples of most common plastic polymer types.

Table 1
Chronological summary of the most relevant studies that report the analysis of MPs in beach sand and the identification of their composition (from most recent to oldest). The MPs were quantified as number of MPs per kg or g /m^2 or m^3 of sand depending on the way they are presented in the original reference. Some exceptions are explained in the table.

Location	Pre- treatment	Extraction	Detection	Amount of MPs	Reference
Gujarat state, India	Drying (104°C) Sieving	Density Separation (NaCl)	Stereomicroscopy ATR-FTIR	Mean: 1.4–26 MPs/kg	[25]
Coral reefs in Palau, Republic of Palau	Removal of large debris Drying (90°C) Grounding Sieving	Density Separation (NaCl) Filtration (pre-weighed filter paper 10–13 μm pore size) Digestion on the filters (30% H_2O_2 + Fe II) Filtration (hydrophilic polycarbonate 0.2 μm membrane filter)	Nile Red staining Epifluorescence microscopy	0.17–32.13 MPs/g	[26]
Taghazout coast, Morocco	Drying (40°C)	Density Separation (NaCl) Filtration (0.45 μm nitrocellulose filter)	ATR-FTIR	915 MPs/kg in 2018 1448 MPs/kg in 2019	[27]
Qingdao coast, China	Drying (Room Temp)	Density Separation ($ZnCl_2$) Filtration (5-μm nitrocellulose membrane) Digestion (30% H_2O_2)	μ–FTIR	3602 ± 1708 MPs/kg	[8]
Kuakata Beach, Bangladesh	Drying (90°C)	Density Separation ($ZnCl_2$) Sieving Drying Digestion (30% H_2O_2 + $FeSO_4$) Filtration (5.0 μm of nitrocellulose filter)	Stereomicroscopy FTIR	232 ± 52 MPs/kg	[28]
Marine beaches, Netherlands	Drying (Room Temp) Sieving	Depolymerization of PET with ethylene glycol	LC-UV (Poroshell 120 Phenyl Hexyl column, MeOH: H_2O)	<0.4 μg/g	[29]
Baltic Sea shore, Poland	Drying (60°C) Sieving Removal of large debris	Density Separation ($ZnCl_2$) Filtration (polyamide filter funnel with 174 μm mesh) Digestion [H_2O_2 (30%) at 75 C] Calcite removal (HCl) Density Separation ($ZnCl_2$) Filtration (polyamide filter funnel with 174 μm mesh) Drying	Stereomicroscopy Raman	Mean: 68 ± 11 MPs/kg	[9]
Mauritius beaches, Mauritius	Drying (Room Temp) Sieving	Density Separation (NaCl)	ATR-FTIR	38.4–196 MPs/m^2	[30]
UNESCO Can Gio Mangrove Biosphere Reserve, Vietnam	Drying (50°C) Removal of large debris	Density Separation (NaCl) Digestion (30% H_2O_2) Filtration (1.6-μm glass-fibre membrane)	Raman	31.99–92.56 MPs/g	[31]
Adelaide, Australia	Sieving	Density Separation (SMI unit, NaCl)	Stereomicroscopy FTIR	0.5 ± 0.1 MPs/kg	[32]
South eastern beaches, Brazil	Sieving	Manual Separation	HSI-NIR	745 MPs/4 m^2	[33]
Southwest Atlantic seaside resort, Argentina	Drying (60°C) Sieving	Density Separation ($CaCl_2$) Filtration (1.2 μm glass fiber filter)	Stereomicroscopy with UV light	184 - 1061 MPs/sampling site	[34]
Tarragona coast, Spain	Drying (40°C) Sieving	Two-step density separation (NaCl, $ZnCl_2$)	Stereomicroscopy ATR-FTIR	<54 MPs/kg	[35]
SE Gulf of California, USA	Drying (<60°C) Sieving	Density Separation (NaCl) Filtration (cellulose 0.45 μm MF-Millipore membrane)	Stereomicroscopy ATR-μ–FTIR	0.31–6.87 MPs/kg	[36]
Karnataka coast, India	Drying (65°C) Sieving	Digestion (30% H_2O_2) Density Separation (NaCl) Filtration (cellulose Whatman GRADE 1 filter)	Stereomicroscopy Red Nile Staining Epifluorescence microscopy Raman spectroscopy FESEM-EDX	200 - 1150 MPs/kg	[37]
Calicut beach, India	Drying (60°C) Sieving	Visual sorting	Stereomicroscopy ATR-FTIR	80.56–467.13 MPs/kg	[38]
Southeast and northeast beaches, Brazil	Drying (60°C)	Two-step density separation (NaCl, $ZnCl_2$) Drying	Stereomicroscopy	2.4–30.4 MPs/m^2	[39]
Beaches at Bristol Channel, UK	Drying (75°C) Sieving	Visual sorting	ATR-FTIR	0.8–132.8 MPs/m^2	[40]
Puerto Rico	Drying (65, 90°C) Sieving	Density Separation (NaCl) Sieving Cascade	ATR-FTIR	3 - 17 MPs/kg	[41]
Marina Beach, India	Drying (60°C) Sieving	Digestion (30% H_2O_2) Density Separation (NaI) Filtration (Whatman grade GF/C filter)	Stereomicroscopy SEM- EDX FTIR	20 - 1540 MPs/kg	[42]
Marina di Vecchiano, Tuscany, Italy	Homogenization Sieving	MAE (DCM)	EGA – Py-GC-MS Double-shot Py-GC–MS (HP-5MS capillary column, 50 °C–700 °C, SIM)	0.003–0.2 g/350 g	[43]
Southern and Northeast, Brazilian	Drying (Room Temp) Sieving	–	HSI-NIR SICMA model Chemometrics	56 MPs/166 g	[44]

(*continued on next page*)

Table 1 (*continued*)

Location	Pre- treatment	Extraction	Detection	Amount of MPs	Reference
Inner Oslofjord, Norway	Removal of large debris	Density Separation Two-step digestion (NaOH/urea/thiourea & 30% H2O2/1%NaOH)	Polarization microscopy ATR-FTIR	338 - 1270 MPs/kg	[45]
Panhandle of Florida, USA	Sieving Drying (50°C)	Density Separation ($CaCl_2$) Filtration (cellulose Whatman GRADE 1 filter)	Stereomicroscopy	2.4–2.8 MPs/kg	[46]
Curonian spit national park, Russia	–	Density Separation ($ZnCl_2$) Digestion (H_2O_2 (30%) + Fe II at 75°C)	Raman	Mean: 46 ± 22 MPs/kg	[47]
Beach in Aveiro, Portugal	–	Density Separation (NaCl) Filtration (0.45 μm mixed cellulose esters filters)	ATR-FTIR	Mean: 22 MPs/kg	[48]
Shilaoren beach, Qingdao, China	Sieving Drying (60°C)	Density Separation (NaCl) Filtration (0.7 μm size filter paper)	Stereomicroscopy FTIR	Mean: 56 MPs/kg	[49]
Macajalar Bay, Philippines	Drying (50°C) Sieving	Density Separation (NaCl) Filtration (0.4 μm Whatman 969 filter) Filter Drying (50°C)	Hot needle test Microscopy	5-8 surface sand litter/sampling site	[50]
Coral reef island, South China	Sieving	Acid Digestion (HNO_3, HCl) Density Separation (CHKO2) Filtration (1.2 μm GF/C filter membranes)	Stereomicroscopy μ–Raman	60 - 610 MPs/kg	[51]
The Mar Menor lagoon, SE Spain	Drying (60°C) Sieving	Density Separation (NaCl) Filtration (Büchner funnel using paper filter)	Microscopy FTIR	8.2–166.3 MPs/kg	[52]
Indian coast, India	Freeze-drying Sieving	Density Separation ($CaCl_2$) Digestion (H_2O_2) Filtration (4′,6-diamidino-2-phenylindole (DAPI), fluorescein isothiocyanate (FITC) and Texas red filter for Epifluorescence Microscopy)	Red Nile staining Epifluorescence Microscopy FTIR SEM-EDX	45 - 220 MPs/kg	[53]
Scarborough & Reighton beaches, UK	Drying (70°C) Removal of large debris	Density Separation ($ZnCl_2$) Sieving Filtration (cellulose Fisherbrand QL100 filter)	Hot-stage microscopy- DART MS	PE & PS MPs detected Not quantified	[54]
Southern beaches, Sri Lanka	Sieving	Density Separation (NaCl)	Raman ATR-FTIR	6 - 738 MPs/kg	[55]
Cyprus	Drying (Room Temp) Sieving	Visual sorting	Visual inspection	637 - 131,939 MPs/m^3	[7]
Tuscany beach, Italy	Homogenization Sieving to remove large debris Drying (60°C) Sieving	Kumagawa-type extraction: 1.Refluxing DCM 2. Refluxing xylenes (135–140 °C)	GPC-DAD & FLD(MIXED-E Mesopore columns, chloroform)	18.7–327.0 mg/kg	[56]
Marina di Vecchiano, Tuscany, Italy	Homogenization Sieving to remove large debris Drying (60°C) Sieving	Kumagawa-type extraction: 1.Refluxing DCM 2. Refluxing xylenes (135–140 °C)	FTIR Py-GC–MS (HP-5 ms capillary column, 40 °C-300 °C) GPC-UV (PLgel Mixed-D columns, chloroform) ^{1}H NMR	5.9–30.2 mg/kg	[57]
4 islands of the Lesser Antilles, United States, United Kingdom, Netherlands, and France	Sieving Drying (60°C)	Density Separation (NaCl) Filtration (cellulose 0.45 μm pore filter)	Stereomicroscopy	130 - 239 MPs/kg	[58]
20 beaches along the coast, Korea	Sieving Visual sorting	Density Separation (LMT) Digestion (35% H_2O_2 and Fe (II), 75°C) Density Separation (NaCl) Filtration (polycarbonate filter)	μ–FTIR	0 - 2088 MPs/m^2 (Large MPs) 1400 - 62,800 MPs/m^2 (Small MPs)	[59]
Isle of Rügen (Baltic Sea), Germany	–	Digestion (H_2O_2 50%, 7 days & NaClO, 24 h) Wet Sieving Density Separation (Glass Elutriation Column) Filtration (glass fibre filters)	Nile red stain dissolved in chloroform Digital image analysis (UV)	Mean: 88.10 MPs/kg	[60]
Gulf of Mexico loggerhead recovery unit, Mexico	Removal of large debris	Density Separation (NaCl) Sieving of the visible MPs Addition of 10% HCl	Stereomicroscopy	Mean: 61.08 ± 34.61 MPs/m^2	[61]
Plastic Fragments found in the sand, France	Manual separation	–	Stereomicroscopy Raman Py-GC–MS(RXi-5 ms® column, 40 °C–320 °C)	Only qualitative analysis	[62]
Beaches of the Baltic Sea in Kaliningrad region, Russia	Drying (Room Temp) Sieving Visual Separation	Density Separation ($ZnCl_2$) Filtration (filter with 174 μm mesh) Digestion (H_2O_2 (30%) + Fe II at 75°C)	Stereomicroscopy	0.2–175.3 MPs/kg	[63]
Meijendel beach, Netherlands	Drying (60°C)	Density Separation (NaCl) Filtration (cellulose 0.45 μm pore filter)	Stereomicroscopy	8 - 38 MPs/kg	[64]

drying at room temperature [67,71,73] and drying in the oven with the temperature from 45 to 90°C are mostly reported [65,66,93]. Plastic polymers are quite resistant to degradation at these temperatures since their melting point is higher than 115°C [25]. However, the temperatures primarily used do not exceed 60°C to ensure the preservation of MPs integrity. The employment of a cascade of sieves of different sizes has been widely described as a way to separate sand and sediment fractions, and thus, MPs by particle size [26,40,93]. Moreover, in samples where the plastic contamination can be observed by naked eye, manual removal of large plastic debris is also done as a pre-treatment

Table 2
Chronological summary of the most relevant studies that report the analysis of MPs in marine sediments and the identification of their composition (from most recent to oldest). The MPs were quantified as number of MPs per kg or g /m^2 or m^3 of marine sediments depending on the way they are presented in the original reference. Some exceptions are explained in the table.

Location	Pre- treatment	Extraction	Detection	Number of MPs	Reference
Tropical lakes, Brazil	Drying (60°C) Wet- washing on 63 μm mesh sieve to keep just the sand	Digestion (10% H_2O_2)	Stereomicroscopy Hot-needle test FTIR	Fragments: 6.3 ± 11.3 MPs/300 g Fibres: 21.25 ± 12.7 MPs/300 g	[65]
Haizhou Bay, China	Drying (65°C)	Density Separation (NaCl, $MnSO_4$) Filtration (mixed fiber 0.45 μm pore membrane)	Stereomicroscopy FTIR	30.89 ± 11.56 MPs/g	[66]
Moheshkhali channel of Bay of Bengal, Bangladesh	–	Density Separation ($ZnCl_2$) Digestion (H_2O_2) Filtration (0.45 μm pore GF/F Whatman filter)	FTIR	6.66–138.33 MPs/m^2	[67]
Buriganga River, Bangladesh	Drying (60°C)	Digestion (30% H_2O_2) Density Separation (NaCl, $ZnCl_2$)	Stereomicroscopy FTIR SEM-EDX	3.5–8.17 MPs/g	[68]
Anzali Wetland, Iran	Drying (Room Temp) Sieving	Digestion (30% H_2O_2) Density Separation ($ZnCl_2$) Filtration (ashless cellulose grade 589/3 blue ribbon, 2 μm pore filter)	Polarization Microscopy Raman SEM - EDX	30 - 1380 MP/kg	[69]
Guanhai Promenade, China	–	Two phase separation (Ethyl acetate: H_2O or 3.5% NaCl)	Confocal Raman Stereomicroscopy	133 ± 33 MPs/kg	[70]
Central Caribbean, Colombia	Drying (Room Temp) Sieving	Density Separation (NaCl) Filtration (gridded mixed cellulose ester filter)	Stereomicroscopy	160 - 1120 MPs/kg	[71]
Mangrove forest, Fuli Mangrove Bay and Yingbin Inland Sea, China	Drying (60°C)	Digestion (30% H_2O_2) Density Separation (CHKO2) Filtration (1.2 μm GF/C glass microfiber filter)	Stereomicroscopy Raman	67 - 203 MPs/kg	[72]
Guanhai Promenade, China	–	Digestion (30% H_2O_2) Two phase separation (Ethyl acetate: H_2O)	Confocal Raman Optical microscopy	156 ± 19 MPs/kg	[70]
Pra and Ankobra estuaries, Ghana	Drying (Room Temp) Crushing Sieving	Digestion (30% H_2O_2) Density Separation ($ZnCl_2$) Centrifugation Filtration (Whatman GF 1.6 μm pore filter)	Stereomicroscopy	Pra: 728 MPs/10 g Ankobra: 456 MPs/ 10 g	[73]
Haller's Round Ray in the Gulf of California, USA	Drying (50°C) Sieving	Digestion (30% H_2O_2) Density Separation (NaCl) Filtration (Whatman GF/B microfiber 1.0 μm pore filter) Filter drying (60°C)	ATR-FTIR	3.58 MPs/kg	[74]
Coral reefs in Palau, Republic of Palau	Removal of large debris Drying (90°C) Grounding Sieving	Density Separation (NaCl) Filtration (pre-weighed filter paper) Digestion on the filters (30% H_2O_2 + Fe II) Filtration (black 0.2 μm isopore filter)	Nile Red staining Epifluorescence microscopy	0.17–32.13 MPs/g	[26]
Qingdao coast, China	Drying (Room Temp)	Digestion (30% H_2O_2) Density Separation ($ZnCl_2$) Filtration (5-μm nitrocellulose membrane)	μ–FTIR	4577 ± 2902 MPs/kg	[8]
Kodaikanal Lake, India	Drying (50°C) Sieving	Digestion (30% H_2O_2) Density Separation ($ZnCl_2$) Filtration (0.8 μm nitrocellulose filter)	Stereoscopy ATR-FTIR SEM-EDX	28.31 ± 5.29 MPs/kg	[75]
Tecolutla beach, Mexico	Drying (60°C) Homogenization Sieving	Density Separation (NaCl) Filtration (cellulose 0.45 μm pore filter)	Stereomicroscopy SEM	27- 720 MPs/kg	[76]
Northeastern Mediterranean shoreline, Turkey	Drying (45°C)	Density Separation ($ZnCl_2$) Filtration (GF/C filter) Digestion (H_2O_2)	Red Nile staining Epifluorescence microscopy ATR-FTIR	118 - 1688 MPs/kg	[77]
Villerest Reservoir, Loire River, France	Removal of leaves and wood fragments Drying Homogenization	Digestion (30% H_2O_2) Density Separation (NaI) Digestion (H_2O_2) Filtration (Anodisc 0.2 μm filter)	μFTIR	0.7–1.6103 MPs/kg	[78]
Hainan Island, China	Drying (60°C) Sieving	Digestion (30% H_2O_2) Density Separation (CHKO2) Filtration (GF/C microfiber 0.45 μm pore filter)	UV–Vis Raman X-ray photoelectron spectroscopy (XPS)	38 - 82 MPs/kg	[79]
Chi River Basin, Thailand	–	Density Separation (NaCl) Filtration (GF/C microfiber 0.45 μm pore filter)	ATR-FTIR	0–15.6 MPs/kg	[80]

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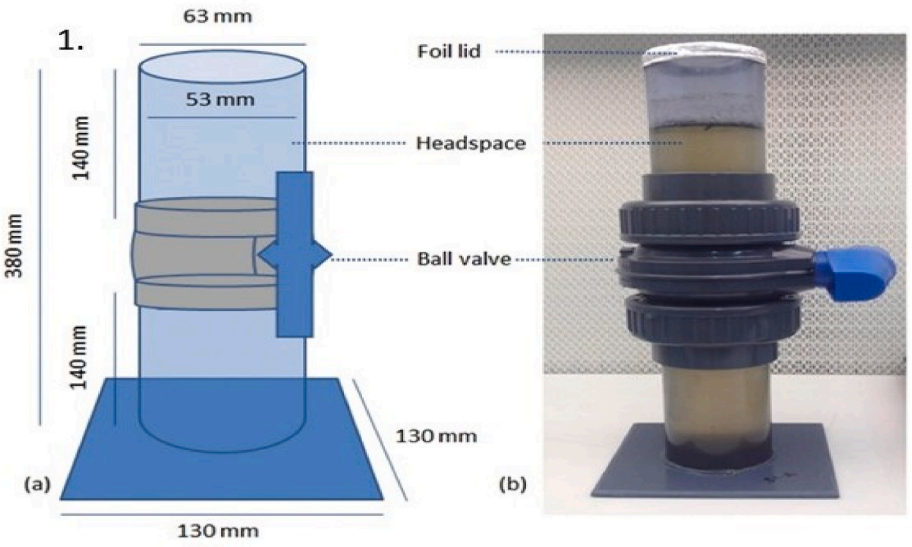
Table 2 (*continued*)

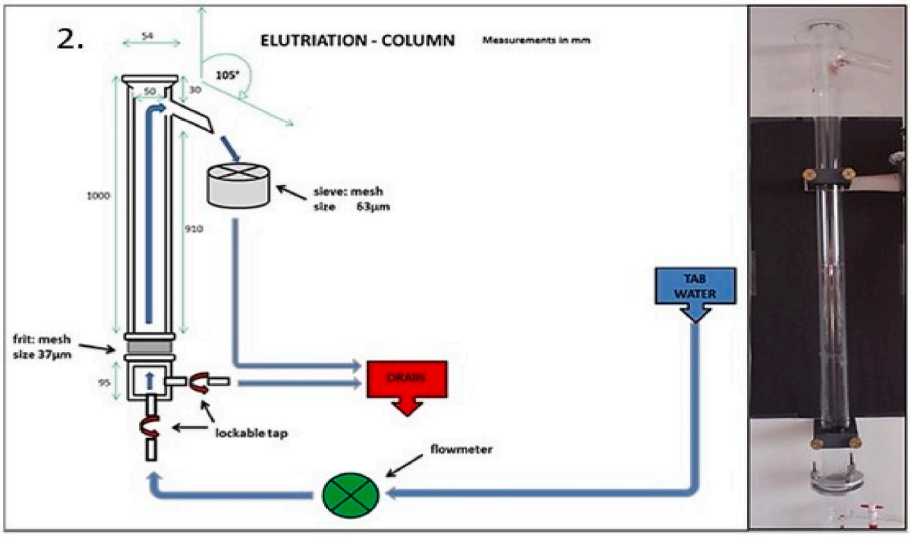
Location	Pre- treatment	Extraction	Detection	Number of MPs	Reference
		Digestion (H_2O_2) Filtration (GF/C microfiber 0.45 μm pore filter)			
Montenegrin coast (Adriatic Sea), Montenegro	Drying	Density Separation (NaCl) Filtration (steel wire sieve with 63 μm pore)	ATR-FTIR	Mean: 63 ± 130.1 MPs/kg	[81]
St. Andrew Bay, Florida	Sieving	Density Separation (NaI) Digestion (H_2O_2 (30%) + Fe II at 75°C) Filtration (cotton 2.7 μm pore fiber)	Stereomicroscopy Raman	3.16–34.03 MPs/kg	[82]
Palu Bay, Central Sulawesi, Indonesia	Drying (90°C)	Density Separation (NaCl) Filtration (metallic sieve) Digestion (30% H_2O_2)	Stereomicroscopy	40.68 ± 10.8 MPs/kg	[83]
Reef platforms in Kepulauan Seribu, Indonesia	Drying (70°C) Sieving	Density separation (SMI unit, NaCl) Filtration (Filter type not specified)	Stereomicroscopy SEM ATR-μ–FTIR	Mean: <99 MPs/kg	[84]
Tarragona coast, Spain	Drying (40°C) Sieving	Two-step density separation (NaCl, $ZnCl_2$)	Stereomicroscopy ATR-FTIR	5 - 89 MPs/kg	[35]
SE Gulf of California, USA	Freeze-drying Sieving	Density Separation ($ZnCl_2$) Filtration (cellulose 0.45 μm MF-Millipore membrane)	Stereomicroscopy ATR-μ–FTIR	40 - 782 MPs/m^2	[36]
Água Branca stream basin, Brazil	Drying (Room Temp) Sieving	Digestion (30% H_2O_2)	Stereomicroscopy	10 - 5160 MPs/kg	[85]
Barra beach, Aveiro, Portugal	Drying (40°C) Sieving	Density Separation (NaCl) Digestion (10% KOH) Filtration (cellulose 7–9 μm pore Prat DUMAS, Flat filter)	Stereomicroscopy ATR-FTIR	100 MPs/kg	[86]
Marina Beach, India	Drying (60°C) Sieving	Digestion (30% H_2O_2) Density Separation (NaI) Filtration (Whatman grade GF/C filter)	Stereomicroscopy SEM- EDX FTIR	60 - 1620 MPs/kg	[42]
Haihe River, China	Drying (Room Temp)	Digestion (30% H_2O_2) Density Separation (NaCl) Filtration (Whatman grade GF/C filter)	Stereomicroscopy μ–FTIR	4980 ± 2462 MPs/kg	[87]
Setiu Wetland, Malaysia	Drying (Room Temp)	Density Separation (NaCl) Filtration (0.45 μm nitrocellulose membrane filter)	SEM Py–GC–MS(Ultra Inert column)	5.97 MPs/g	[88]
Sublittoral area north-west of Leghorn (Tuscany), Italy	Drying (Room Temp) Sieving	[1] Kumagawa-type extraction: i. Refluxing DCM ii. Refluxing xylenes (135–140 °C) [2] Addition of HCl	ATR-FTIR Double- shot Py-GC–MS (50 °C–300 °C) HPLC- UV, DAD, FLD (RP, MeOH/H_2O)	0.0489–1523 mg polymer/kg	[89]
Inner Oslofjord, Norway	Removal of large debris	Density Separation Two-step digestion (30% H2O2/1% NaOH)	Polarization microscopy ATR-FTIR	240 - 1500 MPs/kg	[45]
Seaflower Biosphere Reserve, Caribbean Sea, Colombia	–	Density Separation Addition of 10% HCl	Stereomicroscopy	Mean: 0.5 MPs/m^2	[90]
Southern Mangroves, China	Drying (Room Temp) Sieving	Density Separation ($ZnCl_2$) Digestion (H2O2) Filtration (cellulose 0.45μmpore filter)	Stereomicroscopy μ–Raman	227 - 2249 MPs/kg	[91]
Tiranë, Albania	Sieving	Density Separation ($ZnCl_2$) Digestion (35% H_2O_2)	μ-FTIR	2 MPs/sample	[92]
The Mar Menor lagoon, SE Spain	Drying (60°C) Sieving	Density Separation (NaCl) Filtration (Büchner funnel using a paper filter)	Microscopy FTIR	8.2–166.3 MPs/kg	[52]
Bama Resort, Baluran National Park, Indonesia	Sieving Drying (90°C)	Density Separation (NaCl) Sieving (0.3 mm)	Microscopy	116.41 ± 80.78 MPs/kg	[93]
Lamongan, Indonesia	Drying (60°C) Sieving	Density Separation (NaCl) Sieving (0.3 mm)	Microscopy	Mean: 206 MPs/kg	[94]
Faafu Atoll, Maldives	Drying (60°C) Sieving	Two-step density separation (NaCl, NaI) Filtration (Whatman anodisc filters)	Stereomicroscopy ATR-FTIR	22.8 ± 10.5 MPs/m^2	[95]
Northern Adriatic Sea, Italy & Slovenia	Homogenization Visual sorting	Density Separation (NaCl) Filtration (Büchner funnel using 10 μm pore filter)	Microscopy	137 - 703 MPs/kg	[96]
Baltic bottom, Russia	Homogenization by stirring	Density Separation ($ZnCl_2$) Digestion (H_2O_2 (30%) + Fe II at 75°C) Calcite fraction digestion	Stereomicroscopy	34 ± 10 MPs/kg	[97]
Plymouth Sound Breakwater, Estuary and Portwrinkle Beach, UK	Drying (50°C)	Density Separation (SMI unit: NaCl, NaI, $ZnCl_2$) Sieving (30 μm nylon mesh)	FTIR	29.3–144.1 MPs/kg	[98]

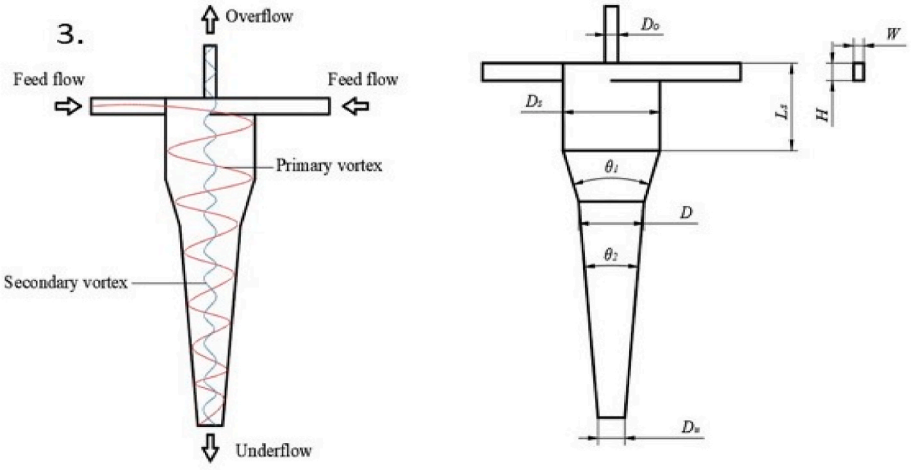
before sample analysis [31,45,54,61].

2.2. Extraction methods associated with visual detection of MPs

Most of the reported procedures for sand and sediments (see Tables 1 and 2) have taken as a basis the National Ocean and Atmospheric







(a) Layout drawing (b) Geometry parameters

Fig. 2. (1) Schematic (a) and photograph (b) of Sediment-Microplastic Isolation (SMI) unit. Photograph depicts SMI unit within contamination control cabinet with ball valve in closed position, denser sediment settled at the bottom of $ZnCl_2$ solution (1.5 g cm−3) and less dense particles floating on top, reproduced by Ref. [1] with permission by Elsevier, (2) Schematic representation of the elutriation column (left) and picture of the elutriation column (right), reproduced by Ref. [2] with permission by Elsevier and (3) Schematic of the hydrocyclone, reproduced by Ref. [3] with permission by Elsevier.

Administration (NOAA) guidelines. These guidelines involve two density separations interrupted by the oxidation of organic matter [24,99]. Multiple variations of this approach have been reported including some new tools that have facilitated the extraction since the traditional NOAA methods tend to have limitations and can result in MP losses [24].

2.2.1. Density separation

Density separation (flotation) is an easy and quick method highly applied to the isolation of MPs from sand and sediment samples. The use of a saturated saline solution creates the condition for the separation of the MPs (light) from the sand/sediment particles (heavy). Different salts have been suggested for the floatation procedure [20]. Sodium chloride (NaCl) is typically utilized since it is cost-effective (1 kg costs approx. 1€) and non-toxic [36,37,48–50]. However, the maximum density reached by this solution (1200 kg/m^3) is not high enough to extract the denser MPs in sand and sediments [100]. Other salts that have been reported to achieve higher densities include sodium iodide (NaI), zinc chloride ($ZnCl_2$), calcium chloride ($CaCl_2$), manganese (II) sulfate ($MnSO_4$) and potassium formate ($CHKO_2$). They, however, are more expensive and toxic, and thus require more careful handling [8,25,34,42,51]. The selection of the salt depends primarily on the density of the plastic polymers of interest and the available laboratory resources [20].

Density separation shows two main problems. The first requirement is to find a method that prevents the sediment settled at the bottom from falling onto the filter during the decantation of the supernatant. Interestingly, to address this issue, Hayes et al. [32] reported the effectiveness of a Sediment-Microplastic Isolation (SMI) unit, a manually constructed device to help the floatation process with NaCl that is described as a compact device that can be easily transported. It facilitates the separation of different solids within the matrix. This SMI unit was mentioned first by Coppock et al. [98] who used three different salts (NaCl, NaI, $ZnCl_2$) for the determination of MPs from Plymouth Sound Breakwater, Estuary and Portwrinkle Beach (UK) sediment samples. The primary material used in SMI is PVC due to its cost-effectiveness, resistance and durability, which promoted the reproducibility of the results (Fig. 2). However, as the own authors recognized, the use of PVC for MPs analysis may pose a significant long-term drawback if degradation occurs. To solve this problem, they proposed regular inspection and utilization of procedural blanks [98].

The second issue, as previously noted, is that NaCl lacks the ability to extract all types of plastics. Contrarily, salts that offer denser solutions and greater extraction efficiency are prohibitively expensive and pose risks of toxicity to both humans and the environment. Two-step density separation using distinct salts has also been performed to increase the extracted MPs, minimizing the use of expensive and toxic salts [35,39]. In other studies that focus on obtaining greener analytical methods, devices based on elutriation or air-induced overflow (AIO) techniques were employed [60,101–103]. Elutriation, first reported in 2013 by Claessens et al. [100], is a method used to separate MPs from sediment. It involves injecting a countercurrent of water, which brings the MPs to the surface independently of their density while the sediment remains at the bottom. The elutriation device, like the previously mentioned SMI unit, is constructed with cost-effective PVC. However, the salt used in elutriation is NaI, which is seven times more expensive than NaCl. To mitigate this additional cost, the authors suggest employing a fluidized sand-bath with a small volume of NaI [104]. AIO is basically based on the same principle but using a countercurrent of air to separate MPs, which requires a complex and sophisticated design mostly developed thanks to 3D printers (Fig. 2). The primary challenge of both techniques lies in the considerable difficulty of adjusting precisely the conditions to achieve an effective MPs separation.

2.2.2. Digestion

In general, sand is considered a “cleaner” matrix than sediment because its organic matter content is lower. For this reason, digestion of the samples is not always necessary [25,27,30,32], while for sediments is widely used [67,68,73,74,77,78,82]. If flotation was able to separate completely the MPs from the matrix, it would remove the digestion step, leading to the elimination of additional reagents and associated costs. The organic matter digestion is mostly performed by the addition of 30% H_2O_2 solution or 30% H_2O_2 + Fe^{2+} at 75°C [9,26,31,47,63,70]. Potassium hydroxide (KOH) is also common [86]. The digestion step can be done either directly on the sample [79] or on the MPs after their extraction (before or after the density separation step) [26]. For the direct digestion of sand, hydrochloric acid (HCl) and nitric acid (HNO_3) are the most commonly employed acids [51,61]. Zhang et al. [51] provided a notable example of their use in the determination of MPs in coral sand. This matrix, which contains a substantial amount of carbonates, was dissolved by these reagents along with the organic matter. Olsen et al. [45] described a two-step digestion protocol for the analysis of MPs in sediment. The first step involved adding a solution containing 8% sodium hydroxide (NaOH), 8% urea, and 6.5% thiourea to dissolve cellulosic materials from the sediment. The second step consisted of adding a 30% H_2O_2 and 1% NaOH solution. This digestion protocol was implemented after the density separation of MPs, which had been filtered using paper filters. The addition of NaOH in the protocol aimed to increase the pH and promote the formation of free radicals, thereby enhancing the digestion of humic and lignin compounds in the samples [45]. Following centrifugation, the supernatant solution was filtered onto black isopore filters and stained with Red Nile dye for MPs quantification using an epifluorescence microscope.

2.2.3. The importance of the filtration step depending on the visualization technique

Filter selection is important even when the determination of MPs is made through visual inspection. While most filters are compatible with various types of optical microscopy, caution must be exercised to prevent the filters from introducing plastic fibers or other natural contaminants, such as cellulose acetate, into the sample. These materials may be susceptible to deterioration from the extraction reagents used. For example, Prata et al. [105] reported that cellulose filters were almost completely degraded when exposed to KOH at 50 °C for 1 h, with other treatments being able to provide 5% of weight loss. The choice of an appropriate filter type becomes even more critical when the analytical method for MP analysis relies on μ-FTIR or μ-Raman. Several factors influence the selection of a filter. An important consideration is whether the filter material causes interference with the MP spectra within analysis range. A huge variety of filters has been tested, the most common being the gold coated polycarbonate, silver, silicon and aluminium oxide (Al_2O_3) filters [106,107]. The gold coated polycarbonate ones are the most expensive, they are not completely flat and in Raman analysis there is a possibility to see polycarbonate peaks through the gold coating. However, it is employed in FTIR analysis when working with reflection because of its reflective surface. The silver filters are sometimes preferred to the gold ones since they are a more economic choice and can also be used in reflection mode. The silicone is a rigid material that provides high resolution images when used for FTIR spectroscopy in transmission mode, but it is not recommended for Raman because the silicon peaks can interfere with the spectra. At last, Al_2O_3 particle filters are a less expensive option to work in transmission mode in the μFTIR. Two major drawbacks of these filters are: (i) they are limited to spectra higher than 1250/cm, and (ii) they require delicate handling to avoid breaks due to their fragility. In general, all these types of filters have been tested for MP analysis and the selection of the most suitable type depends mainly on the analytical method to be used and the resources of each laboratory.

2.3. Extraction protocols associated with chromatographic MP analysis

The choice of the analytical tool for MP identification significantly impacts the sample extraction protocol. In the case of chromatographic analysis, the extraction process can differ significantly from the one used

in microscopy. Microscopy requires the MP form to remain intact, while chromatography needs the dissolution of MPs to enable the detection of their monomers. Tian et al. [29] introduced a straightforward and reliable approach to quantify PET MPs in beach sand. The method involved three steps, including depolymerization of PET using ethylene glycol containing zinc acetate at a temperature of 190 °C. The depolymerized MPs were chemically characterized and quantified using liquid chromatography coupled with mass spectrometry (LC-MS). This innovative technique exhibited sufficient sensitivity for PET MPs analysis, and demonstrated high accuracy throughout the experiment due to the robustness of the LC-MS system. Another extraction method successfully identified PS MPs, plastic additives like phthalates together with oxidation products of PE and PP from samples collected from the shoreline of Marina di Vecchiano (Italy). The method employed microwave-assisted extraction (MAE) using dichloromethane (DCM) at 80 °C, which proved to be highly efficient for subsequent MPs analysis using double-shot Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) [43]. Additionally, two studies from the same research group reported a two-step extraction protocol for MPs and their oxidative degradation products from sand by refluxing, first, DCM at 37°C and, second, xylene at 135–140°C to collect the fraction that was not soluble in DCM [57] using a Kumagawa-type apparatus [56,57]. This type of device ensured the slow percolation of the hot solvent used for extraction (37°C) throughout the sample in order to prevent the re-precipitation of fractions that could be less soluble at lower temperatures [57].

3. Determination of MPs in beach sand and sediments

The choice of analytical techniques for characterizing and quantifying MPs is generally not influenced by the environmental matrix, as long as effective separation methods are employed, and organic matter is eliminated. Microscopic techniques have been widely utilized in the field of MP analysis, and are universally available in laboratories, making them the most commonly employed methods [35,40,44]. Chromatography, particularly Py-GC-MS, is another powerful tool widely used for MP analysis [43,57]. Fig. 3 illustrates the prevalence of microscopic techniques in environmental MP analysis.

3.1. Analytical tools based on microscopy for the analysis of MPs

Microscopic observation and quantification of MPs is commonly applied in sand and sediment samples, from simple stereo-microscopy to more robust microscopic techniques such as scanning electron microscopy (SEM) used to quantify suspected MPs. The scientific literature extensively documents the utilization of various combinations of microscopic techniques with analytical methods capable of determining the chemical composition of MPs. These combinations include techniques such as Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDX or SEM-EDS), Microscopy with Fourier Transform Infrared Spectroscopy (μ-FTIR), and Microscopy with Raman Spectroscopy (μ-Raman). Despite recent advancements in the field, many studies have relied only on techniques such as stereo-microscopy, microscopy with UV light, or microscopy with polarized light to observe and characterize the shape, size, and colour of MPs [7,34,39,45,58,61,63,64,69,83,90,97]. Polarization microscopy is based on birefringent properties of anisotropic (light direction-dependent) MPs and serves mainly as a complementary analysis to detect potential plastic degradation [45,69]. Recent studies have mentioned the use of epifluorescence microscopy in conjunction with Red Nile staining to visualize MPs [26,53]. The hot needle test is a supplementary protocol that can be applied with microscopy to distinguish MPs from organic matter [50,65]. The obvious disadvantage of these methods is the inability to characterize the chemical composition of the particles isolated from the samples and, for this reason, more potent tools based on spectroscopy are necessary. A combination of different methods is usually reported with the aim of producing complete information about the plastics.

SEM and its variations are widely applied for MPs analysis, mostly for structural determination [76,84]. Its combination with EDS adds potential to analyze chemical elements and to identify plastic polymer type (better qualitative results) in the samples and estimate their relative abundance (semi-quantitative results). SEM-EDS has been employed for the determination of MPs found in beach sand from India by two different research groups. The application of this analytical technique enabled these groups to verify the presence of MPs in their respective samples and eliminate other materials [42,53]. Additionally, another variation of SEM-EDS is the use of a field emission SEM (FESEM) instead of the conventional one. It is usually preferred to a normal SEM since it increases the image resolution, provides a greater energy range and less electrostatically distorted images. During these last five years, numerous studies have explored the use of FESEM-EDS to obtain clear and more detailed images that facilitate the elemental identification and give quantitative compositional information about the MPs found in sand and sediment samples [37,68,69,74,108].

FTIR and Raman spectroscopy have become the two basic approaches for plastic polymer identification [35,55]. Both are based on the radiation's interaction with molecular vibrations. Their main advantage is that they are not destructive techniques since the MPs

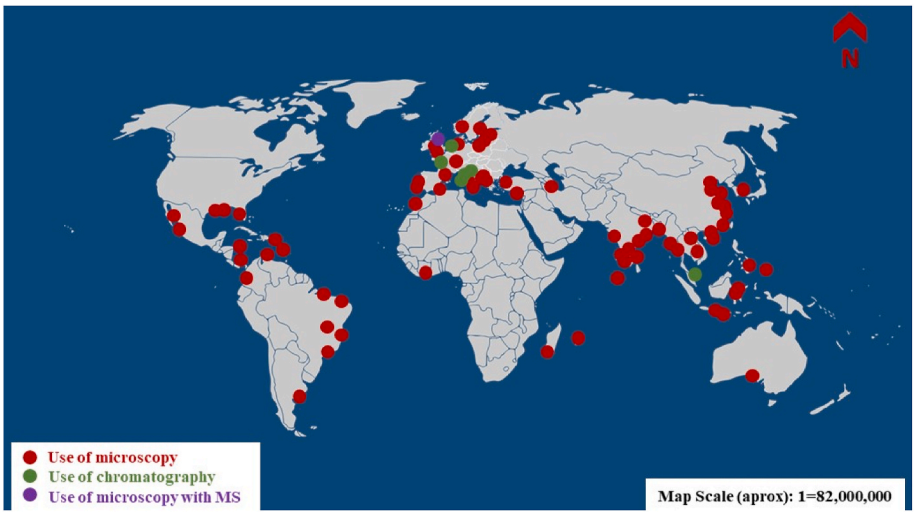


Fig. 3. World map of the analytical methods used in all the references of this review.

isolated, and analyzed, do not undergo any other process or degradation and can, subsequently, be observed with complementary techniques as well [109]. In the case of the FTIR analysis, the three typical operating modes are transmission, reflection, and attenuated total-reflectance (ATR), being the latter the most common since it is able to characterize low size MPs [35,36,45,81,84,86,95]. In the case of ATR, the suspected MP is isolated and placed in optical contact with a crystal to achieve high reflectance. This mode is timesaving and does not require extensive sample preparation but it is not suitable for very small particles that cannot be separated from the filter. Moreover, special attention to the ATR crystal must be paid since it can degrade or break by improper use [109]. The hyphenation of conventional light microscopy with chemical identification by spectroscopy are the most used techniques as they combine the high spatial resolution of the former with FTIR or Raman to provide spatially resolved spectra. No applications of the chemical imaging version of FTIR or Raman, in which the MP image contrast results from the chemical identity of the sample and not just its morphology, have been published. However, these techniques are already commercially available. A novelty worth mentioning is the employment of near infrared (NIR) spectra (780–2500 nm), which is described as a more energetic radiation region, coupled with image analysis in a technique known as near-infrared hyperspectral imaging (HSI-NIR). Like FTIR, it is a non-destructive method that provides advantages in MPs determination from environmental matrices such as intrinsic broader spectral features, higher detectability for direct matrix analysis, and very large datasets with thousands of acquired spectra [44]. To address the last advantage, several chemometric models have been proposed. Vidal & Pasquini [44] suggested the use of HSI-NIR followed by Soft Independent Modelling of Class Analogy (SIMCA) for the automatic and fast identification of five common polymers found in sand [PE, PP, PS, PET and nylon 6/polyamide-6 (PA-6)] with a comprehensive spectral dataset. The method involved chemometric model validation for identifying the type of MP, and it was successfully applied to beach sand samples from Brazil. SIMCA is a supervised classification protocol based on a multidimensional defined space for a specific class, with space limits being defined according to polymer spectra information. The developed method has been validated both by pixel-wise internal validation of the chemometric model and by applying it to assess direct sand analysis and characteristics such as polymer type, size, detectability level, colour, and weathering. The overall system demonstrated reliability in MPs analysis, minimizing false positives, and accurately identifying MPs across the size range of 150 μm to 5 mm [44]. Following the same protocol, Tsukada et al. [33] examined the incidence and composition of MPs on three distinct beaches in Brazil, and further explored the association between MPs abundance and the morphodynamic features of the beach environment.

Ashton et al. [54] discussed a novel methodology for analysing MPs found in beach sand samples from the UK. They introduced a combination of hot-stage microscopy (thermomicroscopy) with real-time mass spectrometry, naming the new system hot-stage microscopy direct analysis in real time (DART)-MS (HDM). The ceramic hot-stage in the ion source allowed for precise temperature control, and the simultaneous microscopy and spectrometry provided both mass spectral and optical data as a function of temperature. The method was validated and successfully applied to real sand samples, enabling qualitative analysis of MP polymers. Unfortunately, a quantitative analysis was not performed (Fig. 4) [54].

3.2. Analytical tools based on chromatography for the analysis of MPs

Chromatography is another powerful tool for MP analysis, although its use is not as common as the use of microscopy methods. The most frequently reported protocols involve a pyrolysis system coupled with GC–MS (Py-GC–MS). This system is characterized by performing three main steps, namely destructuring, separation and identification [110]. The pyrolysis step involves the sample heating at high temperatures (>400°C) to break the chemical bonds of the monomers present, and is needed as a preparation step before the injection of the samples. The potential of this technique is undeniable, providing the entire characterization of a particle with high resolution results [110]. Regarding the determination of MPs in sand and sediment samples during the last five years, Py-GC–MS has been reported, usually accompanied with other analytical methodologies with the aim of obtaining more complete data about the MPs isolated from these matrices [57,88,89]. As it has already been highlighted, harmonized protocols for MPs analysis do not exist up to date and in the case of Py-GC–MS, the optimization of the method is often performed before real sample analysis [62]. For pyrolysis, temperatures of 650 or 700°C are mostly reported, while in the GC oven, the temperature tends to reach 300°C [57,62]. Evolved gas analysis (EGA) and double-shot pyrolysis enhance information are generally employed. EGA eliminates the GC's analytical column, using a gradually increasing pyrolyzer temperature to identify compounds based on their melting points. Double-shot pyrolysis employs two temperature shots: one up to around 350 °C (to elute volatile compounds), and another up to around

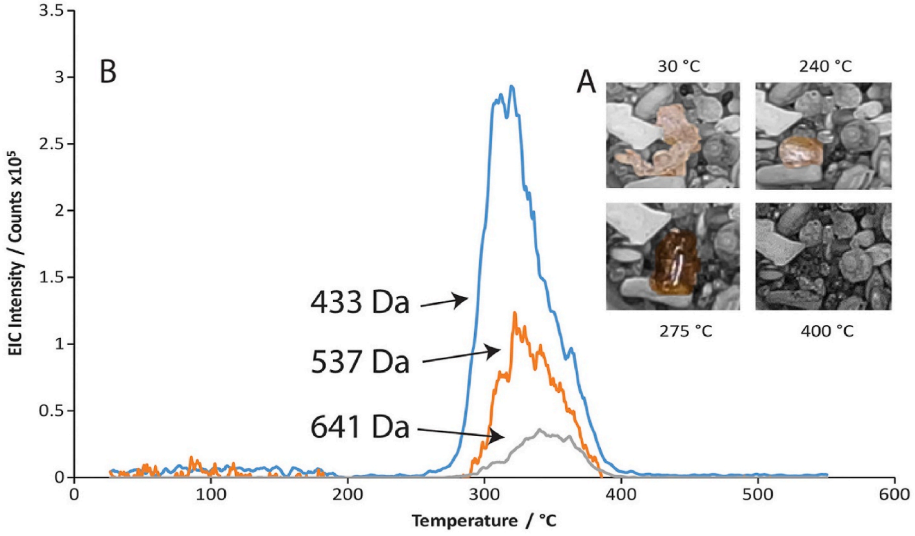


Fig. 4. HDM analysis of flotation products extracted from beach 1. A, Greyscale micrographs showing polymeric species (highlighted in colour) melting; B, EIC profiles of selected polystyrene oligomers plotted as a function of temperature, *m/z* 433 $[C33H36 + H]^+$. Reproduced by Ref. [4] with permission by Elsevier.

600 °C (to decompose the polymer into its monomers) [43,89]. Reported Py-GC-MS analyses used a single quadrupole mass analyzer [39,53,58,84,85], requiring an extensive clean-up of the sample for accurate MPs identification. Recently, Py-GC-MS with an Orbitrap detector has been introduced, offering selectivity and untargeted analysis. This system (not applied yet to sand and marine sediment analysis) enables screening of raw data from the quantitation experiment to find additional chemicals resulting from the pyrolysis step [111].

Less common is the employment of liquid chromatographic methods for MPs analysis due to the various challenges it presents, such as the sample extraction. However, studies have reported the use of high-pressure liquid chromatography (HPLC) coupled with different detectors such as UV, fluorescence (FLD) or diode array (DAD). For example, Castelvetro et al. [89] mentioned a great variety of techniques in order to achieve the polymer identification and specific analysis (PISA) of MPs total mass. After a hydrolytic depolymerization process, the extracts are analyzed in a reverse-phase (RP) HPLC using a mix of MeOH and H_2O as mobile phases, while both UV and FLD detectors are utilized, and the polymer amount calculation is based on the calibrated response of both detectors. The reported limits of detection (LOD) and quantification (LOQ) have been calculated using the equation LOD = 3·SD/m = 0.10 μg and LOQ = 10·SD/m = 0.35 μg (with SD: standard deviation of the blank areas, and m: slope of the calibration curve). Moreover, LC-UV is used after a depolymerization protocol for the analysis of PET MPs and NPs from sands, indoor dust and sludge with recoveries around 99 ± 2% and LOQ of 0.4 μg/g, 1 mg/g and 0.2 μg/g, respectively [29].

Last but not least, some well-known but rarely used complementary methods for MPs analysis have been mentioned in recent bibliography. Gel permeation chromatography (GPC) coupled with a double detector (GPC-FLD and DAD) has been reported by Biver et al. [56] for the selective determination of PS and partially degraded polyolefins (LDPEox) plastic polymers. Furthermore, Ceccarini et al. [57] combined an impressive variety of analytical tools from some expected ones, such as FTIR and Py-GC–MS (Fig. 5), to some unexpected ones, such as GPC-UV and even proton nuclear magnetic resonance (^{1}H NMR), for MPs determination in sand samples. The GPC-UV protocol allows the assessment of the molecular weight and the molecular weight distribution of the polymeric fractions from the extracts, whereas the ^{1}H NMR is used as a confirmation technique for the FTIR analysis as the results of both systems were in complete agreement. These two methods identified the polymer types and evaluated the possible structural modifications by weathering conditions proving the complementarity of all of them.

4. Conclusions

Sand and sediments have been studied extensively as they provide valuable information about the plastic debris pollution of coastal environments. The most commonly used protocol for the isolation of MPs from these matrices is density separation, followed by digestion of organic matter. However, extraction with organic solvents able to dissolve plastics is increasingly preferred when chromatographic determination is involved. In methods combining microscopy and Raman or FTIR, the filter material is very important to achieve good results and to exploit the high performance of both techniques combination. In this sense, it is to be expected that in the near future, new, more reflective or more transparent materials will be developed to take advantage of all the possibilities of such combination. Up to date, microscopy is unequivocally the most preferred tool for MPs analysis in beach sand and sediment, with μ-FTIR and μ-Raman being the techniques most commonly used. These last years, the advances in analytical instrumentation have allowed the achievement of lower detection limits, and with the standardization of μ-FTIR and μ-Raman, it is possible to scan the entire filter. It is important to highlight that μ-FTIR allows the detection and identification of MPs with the size of even 5 μm. Further progress is anticipated in the shift from light microscopy combined with FTIR or Raman to faster and more precise imaging techniques, enabling for rapid and accurate identification.

As far as chromatography is concerned, Py-GC–MS application is nowadays increasing due to its usefulness and the huge amount of information it can provide. LC-MS and GPC have been suggested, mostly as complementary methods, although these two techniques based on mass spectrometry or chromatographic mass spectrometry had always been reported as a rarity in MPs analysis. Methods combining LC-MS show promise and are expected to advance significantly in the coming years, potentially becoming essential for complementing visual inspection in achieving accurate identification.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

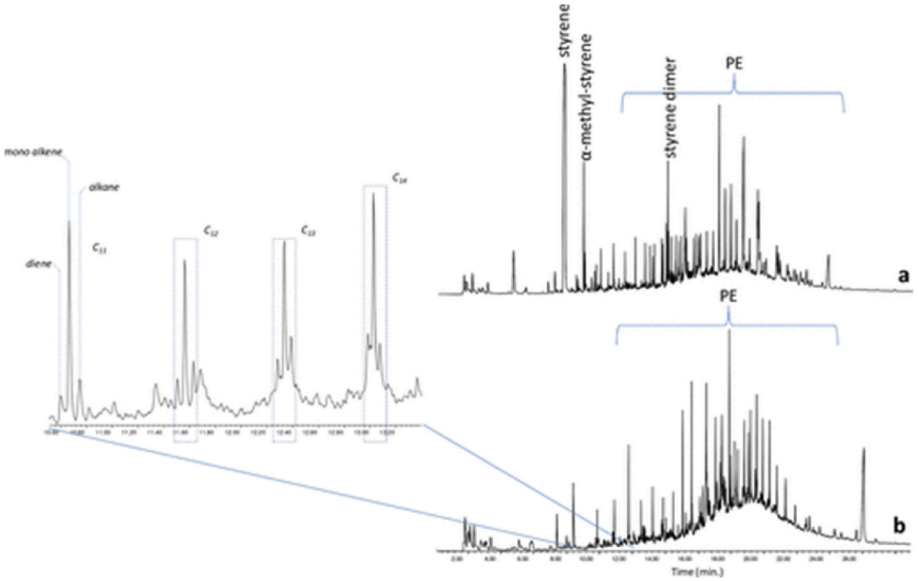


Fig. 5. Chromatograms from the Py-GC/MS analysis of (a) sample G3040001 from sector A (dunes); (b) sample G3040008 from sector D (foreshore). PE = polyethylene pyrolysis products. Reproduced by Ref. [5] with permission by Elsevier.

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Data availability

No data was used for the research described in the article.

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References

[1] J.F. Grillo, A. Guerrero Rebolledo, M.A. Sabino, R. Ramos, Microplastics in Latin America and the Caribbean: on the adoption of reporting standards and quality assurance and quality control protocols, Environ. Adv. 8 (2022), 100236, https://doi.org/10.1016/J.ENVADV.2022.100236.
[2] P. Li, X. Wang, M. Su, X. Zou, L. Duan, H. Zhang, Characteristics of plastic pollution in the environment: a review, Bull. Environ. Contam. Toxicol. 107 (2021) 577–584, https://doi.org/10.1007/s00128-020-02820-1.
[3] E. Curren, V.S. Kuwahara, T. Yoshida, S.C.Y. Leong, Marine microplastics in the ASEAN region: a review of the current state of knowledge, Environ. Pollut. 288 (2021), 117776, https://doi.org/10.1016/J.ENVPOL.2021.117776.
[4] R.C. Thompson, Y. Olsen, R.P. Mitchell, A. Davis, S.J. Rowland, A.W.G. John, D. McGonigle, A.E. Russell, Lost at sea: where is all the plastic? Science 304 (2004) 838, https://doi.org/10.1126/science.1094559 (80-.).
[5] V. Soursou, J. Campo, Y. Picó, Revisiting the analytical determination of PAHs in environmental samples: an update on recent advances, Trends Environ. Anal. Chem. 37 (2023), e00195, https://doi.org/10.1016/j.teac.2023.e00195.
[6] T. Martellini, C. Guerranti, C. Scopetani, A. Ugolini, D. Chelazzi, A. Cincinelli, A snapshot of microplastics in the coastal areas of the Mediterranean Sea, TrAC, Trends Anal. Chem. 109 (2018) 173–179, https://doi.org/10.1016/J.TRAC.2018.09.028.
[7] E.M. Duncan, J. Arrowsmith, C. Bain, A.C. Broderick, J. Lee, K. Metcalfe, S. K. Pikesley, R.T.E. Snape, E. van Sebille, B.J. Godley, The true depth of the Mediterranean plastic problem: extreme microplastic pollution on marine turtle nesting beaches in Cyprus, Mar. Pollut. Bull. 136 (2018) 334–340, https://doi.org/10.1016/J.MARPOLBUL.2018.09.019.
[8] Y. Luo, C. Sun, C. Li, Y. Liu, S. Zhao, Y. Li, F. Kong, H. Zheng, X. Luo, L. Chen, F. Li, Spatial patterns of microplastics in surface seawater, sediment, and sand along qingdao coastal environment, Front. Mar. Sci. 9 (2022), https://doi.org/10.3389/fmars.2022.916859.
[9] E. Esiukova, O. Lobchuk, M. Haseler, I. Chubarenko, Microplastic contamination of sandy beaches of national parks, protected and recreational areas in southern parts of the Baltic Sea, Mar. Pollut. Bull. 173 (2021), 113002, https://doi.org/10.1016/J.MARPOLBUL.2021.113002.
[10] C. Li, R. Busquets, L.C. Campos, Assessment of microplastics in freshwater systems: a review, Sci. Total Environ. 707 (2020), 135578, https://doi.org/10.1016/j.scitotenv.2019.135578.
[11] C. Li, R. Busquets, R.B. Moruzzi, L.C. Campos, Preliminary study on low-density polystyrene microplastics bead removal from drinking water by coagulation-flocculation and sedimentation, J. Water Process Eng. (2021), https://doi.org/10.1016/j.jwpe.2021.102346.
[12] H. Ya, B. Jiang, Y. Xing, T. Zhang, M. Lv, X. Wang, Recent advances on ecological effects of microplastics on soil environment, Sci. Total Environ. 798 (2021), 149338, https://doi.org/10.1016/j.scitotenv.2021.149338.
[13] D. He, Y. Luo, S. Lu, M. Liu, Y. Song, L. Lei, Microplastics in soils: analytical methods, pollution characteristics and ecological risks, TrAC, Trends Anal. Chem. 109 (2018) 163–172, https://doi.org/10.1016/j.trac.2018.10.006.
[14] M.B. Zobkov, E.E. Esiukova, Microplastics in a marine environment: review of methods for sampling, processing, and analyzing microplastics in water, bottom sediments, and coastal slk, Oceanology 58 (2018) 137–143, https://doi.org/10.1134/S0001437017060169.
[15] J.C. Prata, J.P. da Costa, A.C. Duarte, T. Rocha-Santos, Methods for sampling and detection of microplastics in water and sediment: a critical review, TrAC, Trends Anal. Chem. 110 (2019) 150–159, https://doi.org/10.1016/j.trac.2018.10.029.
[16] O.H. Fred-Ahmadu, N.U. Benson, O.O. Ayejuyo, A review of analytical methods used in microplastics quantification, IOP Conf. Ser. Earth Environ. Sci. 665 (2021), 12064, https://doi.org/10.1088/1755-1315/665/1/012064.
[17] S. Jung, S.-H. Cho, K.-H. Kim, E.E. Kwon, Progress in quantitative analysis of microplastics in the environment: a review, Chem. Eng. J. 422 (2021), 130154, https://doi.org/10.1016/j.cej.2021.130154.
[18] Y. Li, Q. Lu, Y. Xing, K. Liu, W. Ling, J. Yang, Q. Yang, T. Wu, J. Zhang, Z. Pei, Z. Gao, X. Li, F. Yang, H. Ma, K. Liu, D. Zhao, Review of research on migration, distribution, biological effects, and analytical methods of microfibers in the environment, Sci. Total Environ. 855 (2023), 158922, https://doi.org/10.1016/J.SCITOTENV.2022.158922.
[19] H. Luo, C. Liu, D. He, J. Sun, J. Li, X. Pan, Effects of aging on environmental behavior of plastic additives: migration, leaching, and ecotoxicity, Sci. Total Environ. 849 (2022), 157951, https://doi.org/10.1016/J.SCITOTENV.2022.157951.
[20] L. Cutroneo, A. Reboa, I. Geneselli, M. Capello, Considerations on salts used for density separation in the extraction of microplastics from sediments, Mar. Pollut. Bull. 166 (2021), 112216, https://doi.org/10.1016/j.marpolbul.2021.112216.
[21] Y. Picó, D. Barceló, Micro(Nano)plastic analysis: a green and sustainable perspective, J. Hazard. Mater. Adv. 6 (2022), 100058, https://doi.org/10.1016/J.HAZADV.2022.100058.
[22] N. Kasmuri, N.A.A. Tarmizi, A. Mojiri, Occurrence, impact, toxicity, and degradation methods of microplastics in environment—a review, Environ. Sci. Pollut. Res. 29 (2022) 30820–30836, https://doi.org/10.1007/s11356-021-18268-7.
[23] J. Porta Casanellas, Edafología para la agricultura y el medio ambiente, 3a. ed., Mundi-Prensa, Madrid, 2003.
[24] L. Rivoira, M. Castiglioni, S.M. Rodrigues, V. Freitas, M.C. Bruzzoniti, S. Ramos, C.M.R. Almeida, Microplastic in marine environment: reworking and optimisation of two analytical protocols for the extraction of microplastics from sediments and oysters, MethodsX 7 (2020), 101116, https://doi.org/10.1016/j.mex.2020.101116.
[25] V. Rabari, K. Patel, H. Patel, J. Trivedi, Quantitative assessment of microplastic in sandy beaches of Gujarat state, India, Mar. Pollut. Bull. 181 (2022), 113925, https://doi.org/10.1016/J.MARPOLBUL.2022.113925.
[26] E. Béraud, V. Bednarz, I. Otto, Y. Golbuu, C. Ferrier-Pagès, Plastics are a new threat to Palau's coral reefs, PLoS One 17 (2022), e0270237, https://doi.org/10.1371/journal.pone.0270237.
[27] M. Ben-Haddad, M.R. Abelouah, S. Hajji, N. Rangel-Buitrago, F. Hamadi, A. A. Alla, Microplastics pollution in sediments of Moroccan urban beaches: the Taghazout coast as a case study, Mar. Pollut. Bull. 180 (2022), 113765, https://doi.org/10.1016/J.MARPOLBUL.2022.113765.
[28] P. Banik, M.B. Hossain, A.-A.U. Nur, T.R. Choudhury, S.I. Liba, J. Yu, M. A. Noman, J. Sun, Microplastics in sediment of Kuakata beach, Bangladesh: occurrence, spatial distribution, and risk assessment, Front. Mar. Sci. 9 (2022), https://doi.org/10.3389/fmars.2022.860989.
[29] L. Tian, E. Skoczynska, D. Siddhanti, R.J. van Putten, H.A. Leslie, G.J.M. Gruter, Quantification of polyethylene terephthalate microplastics and nanoplastics in sands, indoor dust and sludge using a simplified in-matrix depolymerization method, Mar. Pollut. Bull. 175 (2022), 113403, https://doi.org/10.1016/J.MARPOLBUL.2022.113403.
[30] S. Mattan-Moorgawa, J. Chockalingum, C. Appadoo, A first assessment of marine meso-litter and microplastics on beaches: where does Mauritius stand? Mar. Pollut. Bull. 173 (2021), 112941 https://doi.org/10.1016/J.MARPOLBUL.2021.112941.
[31] V.T.K. Khuyen, D.V. Le, A.R. Fischer, C. Dornack, Comparison of microplastic pollution in beach sediment and seawater at UNESCO can Gio mangrove biosphere reserve, Glob. Challenges 5 (2021), 2100044, https://doi.org/10.1002/gch2.202100044.
[32] A. Hayes, P. Kirkbride, S.C. Leterme, Variation in polymer types and abundance of microplastics from two rivers and beaches in Adelaide, South Australia, Mar. Pollut. Bull. 172 (2021), 112842, https://doi.org/10.1016/J.MARPOLBUL.2021.112842.
[33] E. Tsukada, E. Fernandes, C. Vidal, R.F. Salla, Beach morphodynamics and its relationship with the deposition of plastic particles: a preliminary study in southeastern Brazil, Mar. Pollut. Bull. 172 (2021), 112809, https://doi.org/10.1016/J.MARPOLBUL.2021.112809.
[34] M.L. Jaubet, E. Hines, R. Elías, G.V. Garaffo, Factors driving the abundance and distribution of microplastics on sandy beaches in a Southwest Atlantic seaside resort, Mar. Environ. Res. 171 (2021), 105472, https://doi.org/10.1016/J.MARENVRES.2021.105472.
[35] N. Expósito, J. Rovira, J. Sierra, J. Folch, M. Schuhmacher, Microplastics levels, size, morphology and composition in marine water, sediments and sand beaches. Case study of Tarragona coast (western Mediterranean), Sci. Total Environ. 786 (2021), 147453, https://doi.org/10.1016/j.scitotenv.2021.147453.
[36] L.M. Rios-Mendoza, J.F. Ontiveros-Cuadras, D. Leon-Vargas, A.C. Ruiz-Fernández, M. Rangel-García, L.H. Pérez-Bernal, J.A. Sanchez-Cabeza, Microplastic contamination and fluxes in a touristic area at the SE Gulf of California, Mar. Pollut. Bull. 170 (2021), 112638, https://doi.org/10.1016/J.MARPOLBUL.2021.112638.
[37] N.A. Yaranal, S. Subbiah, K. Mohanty, Distribution and characterization of microplastics in beach sediments from Karnataka (India) coastal environments, Mar. Pollut. Bull. 169 (2021), 112550, https://doi.org/10.1016/J.MARPOLBUL.2021.112550.
[38] A.S. Kumar, G.K. Varghese, Microplastic pollution of Calicut beach - contributing factors and possible impacts, Mar. Pollut. Bull. 169 (2021), 112492, https://doi.org/10.1016/J.MARPOLBUL.2021.112492.
[39] I.F.N. Maynard, P.C. Bortoluzzi, L.M. Nascimento, R.R. Madi, E.B. Cavalcanti, Á. S. Lima, V. de L.S. Jeraldo, M.N. Marques, Analysis of the occurrence of microplastics in beach sand on the Brazilian coast, Sci. Total Environ. 771 (2021), 144777, https://doi.org/10.1016/J.SCITOTENV.2020.144777.
[40] D.R. Wilson, B.J. Godley, G.L. Haggar, D. Santillo, K.L. Sheen, The influence of depositional environment on the abundance of microplastic pollution on beaches in the Bristol Channel, UK, Mar. Pollut. Bull. 164 (2021), 111997, https://doi.org/10.1016/J.MARPOLBUL.2021.111997.
[41] K.M. Pérez-Alvelo, E.M. Llegus, J.M. Forestier-Babilonia, C.V. Elías-Arroyo, K. N. Pagán-Malavé, G.J. Bird-Rivera, C.J. Rodríguez-Sierra, Microplastic pollution

on sandy beaches of Puerto Rico, Mar. Pollut. Bull. 164 (2021), 112010, https://doi.org/10.1016/J.MARPOLBUL.2021.112010.
[42] T.G. Sunitha, V. Monisha, S. Sivanesan, M. Vasanthy, M. Prabhakaran, K. Omine, V. Sivasankar, A. Darchen, Micro-plastic pollution along the bay of bengal coastal stretch of Tamil nadu, south India, Sci. Total Environ. 756 (2021), 144073, https://doi.org/10.1016/J.SCITOTENV.2020.144073.
[43] J. La Nasa, G. Biale, M. Mattonai, F. Modugno, Microwave-assisted solvent extraction and double-shot analytical pyrolysis for the quali-quantitation of plasticizers and microplastics in beach sand samples, J. Hazard Mater. 401 (2021), 123287, https://doi.org/10.1016/J.JHAZMAT.2020.123287.
[44] C. Vidal, C. Pasquini, A comprehensive and fast microplastics identification based on near-infrared hyperspectral imaging (HSI-NIR) and chemometrics, Environ. Pollut. 285 (2021), 117251, https://doi.org/10.1016/J.ENVPOL.2021.117251.
[45] L.M.B. Olsen, H. Knutsen, S. Mahat, E.J. Wade, H.P.H. Arp, Facilitating microplastic quantification through the introduction of a cellulose dissolution step prior to oxidation: proof-of-concept and demonstration using diverse samples from the Inner Oslofjord, Norway, Mar. Environ. Res. 161 (2020), 105080, https://doi.org/10.1016/J.MARENVRES.2020.105080.
[46] T.A. Plee, C.M. Pomory, Microplastics in sandy environments in the Florida Keys and the panhandle of Florida, and the ingestion by sea cucumbers (Echinodermata: Holothuroidea) and sand dollars (Echinodermata: echinoidea), Mar. Pollut. Bull. 158 (2020), 111437, https://doi.org/10.1016/J.MARPOLBUL.2020.111437.
[47] I. Chubarenko, E. Esiukova, L. Khatmullina, O. Lobchuk, A. Grave, A. Kileso, M. Haseler, From macro to micro, from patchy to uniform: analyzing plastic contamination along and across a sandy tide-less coast, Mar. Pollut. Bull. 156 (2020), 111198, https://doi.org/10.1016/J.MARPOLBUL.2020.111198.
[48] J.C. Prata, V. Reis, A. Paço, P. Martins, A. Cruz, J.P. da Costa, A.C. Duarte, T. Rocha-Santos, Effects of spatial and seasonal factors on the characteristics and carbonyl index of (micro)plastics in a sandy beach in Aveiro, Portugal, Sci. Total Environ. 709 (2020), 135892, https://doi.org/10.1016/J.SCITOTENV.2019.135892.
[49] R. Pervez, Y. Wang, Z. Jattak, S. Zahir, Z. Yan, D. Zhaoxin, Monitoring of Micro-plastics: a Case Study of Shilaoren Beach, Monitoring of Micro-plastics: a Case Study of Shilaoren Beach, Qingdao, China, 2020, https://doi.org/10.33263/BRIAC101.869875.
[50] M.L. Kalnasa, S.M.O. Lantaca, L.C. Boter, G.J.T. Flores, V.R.K.R. Galarpe, Occurrence of surface sand microplastic and litter in Macajalar Bay, Philippines, Mar. Pollut. Bull. 149 (2019), 110521, https://doi.org/10.1016/J.MARPOLBUL.2019.110521.
[51] L. Zhang, S. Zhang, Y. Wang, K. Yu, R. Li, The spatial distribution of microplastic in the sands of a coral reef island in the South China Sea: comparisons of the fringing reef and atoll, Sci. Total Environ. 688 (2019) 780–786, https://doi.org/10.1016/J.SCITOTENV.2019.06.178.
[52] J. Bayo, D. Rojo, S. Olmos, Abundance, morphology and chemical composition of microplastics in sand and sediments from a protected coastal area: the Mar Menor lagoon (SE Spain), Environ. Pollut. 252 (2019) 1357–1366, https://doi.org/10.1016/J.ENVPOL.2019.06.024.
[53] M. Tiwari, T.D. Rathod, P.Y. Ajmal, R.C. Bhangare, S.K. Sahu, Distribution and characterization of microplastics in beach sand from three different Indian coastal environments, Mar. Pollut. Bull. 140 (2019) 262–273, https://doi.org/10.1016/J.MARPOLBUL.2019.01.055.
[54] G.P. Ashton, L.P. Harding, G.M.B. Parkes, S.E. Pownall, Application of hot-stage microscopy direct analysis in real time mass spectrometry (HDM) to the analysis of polymers, Rapid Commun. Mass Spectrom. 35 (2021), e8522, https://doi.org/10.1002/rcm.8522.
[55] J. Bimali Koongolla, A.L. Andrady, P.B. Terney Pradeep Kumara, C. S. Gangabadage, Evidence of microplastics pollution in coastal beaches and waters in southern Sri Lanka, Mar. Pollut. Bull. 137 (2018) 277–284, https://doi.org/10.1016/J.MARPOLBUL.2018.10.031.
[56] T. Biver, S. Bianchi, M.R. Carosi, A. Ceccarini, A. Corti, E. Manco, V. Castelvetro, Selective determination of poly(styrene) and polyolefin microplastics in sandy beach sediments by gel permeation chromatography coupled with fluorescence detection, Mar. Pollut. Bull. 136 (2018) 269–275, https://doi.org/10.1016/J.MARPOLBUL.2018.09.024.
[57] A. Ceccarini, A. Corti, F. Erba, F. Modugno, J. La Nasa, S. Bianchi, V. Castelvetro, The Hidden microplastics: new insights and figures from the thorough separation and characterization of microplastics and of their degradation byproducts in coastal sediments, Environ. Sci. Technol. 52 (2018) 5634–5643, https://doi.org/10.1021/acs.est.8b01487.
[58] T. Bosker, L. Guaita, P. Behrens, Microplastic pollution on caribbean beaches in the lesser antilles, Mar. Pollut. Bull. 133 (2018) 442–447, https://doi.org/10.1016/J.MARPOLBUL.2018.05.060.
[59] S. Eo, S.H. Hong, Y.K. Song, J. Lee, J. Lee, W.J. Shim, Abundance, composition, and distribution of microplastics larger than 20 μm in sand beaches of South Korea, Environ. Pollut. 238 (2018) 894–902, https://doi.org/10.1016/J.ENVPOL.2018.03.096.
[60] E. Hengstmann, M. Tamminga, C. vom Bruch, E.K. Fischer, Microplastic in beach sediments of the Isle of Rügen (Baltic Sea) - implementing a novel glass elutriation column, Mar. Pollut. Bull. 126 (2018) 263–274, https://doi.org/10.1016/j.marpolbul.2017.11.010.
[61] V.K. Beckwith, M.M.P.B. Fuentes, Microplastic at nesting grounds used by the northern Gulf of Mexico loggerhead recovery unit, Mar. Pollut. Bull. 131 (2018) 32–37, https://doi.org/10.1016/J.MARPOLBUL.2018.04.001.
[62] L. Hermabessiere, C. Himber, B. Boricaud, M. Kazour, R. Amara, A.-L. Cassone, M. Laurentie, I. Paul-Pont, P. Soudant, A. Dehaut, G. Duflos, Optimization, performance, and application of a pyrolysis-GC/MS method for the identification of microplastics, Anal. Bioanal. Chem. 410 (2018) 6663–6676, https://doi.org/10.1007/s00216-018-1279-0.
[63] E. Esiukova, Plastic pollution on the Baltic beaches of Kaliningrad region, Russia, Mar. Pollut. Bull. 114 (2017) 1072–1080, https://doi.org/10.1016/J.MARPOLBUL.2016.10.001.
[64] A. Besley, M.G. Vijver, P. Behrens, T. Bosker, A standardized method for sampling and extraction methods for quantifying microplastics in beach sand, Mar. Pollut. Bull. 114 (2017) 77–83, https://doi.org/10.1016/J.MARPOLBUL.2016.08.055.
[65] J.S. Silva-Cavalcanti, J.C.P. Silva, F.M. de Andrade, A.M.S.S. Brito, M.F. da Costa, Microplastic pollution in sediments of tropical shallow lakes, Sci. Total Environ. 855 (2023), 158671, https://doi.org/10.1016/J.SCITOTENV.2022.158671.
[66] S. Gao, K. Yan, B. Liang, R. Shu, N. Wang, S. Zhang, The different ways microplastics from the water column and sediment accumulate in fish in Haizhou Bay, Sci. Total Environ. 854 (2023), 158575, https://doi.org/10.1016/J.SCITOTENV.2022.158575.
[67] S. Al Nahian, M.R.J. Rakib, R. Kumar, S.M.B. Haider, P. Sharma, A.M. Idris, Distribution, characteristics, and risk assessments analysis of microplastics in shore sediments and surface water of Moheshkhali channel of Bay of Bengal, Bangladesh, Sci. Total Environ. 855 (2023), 158892, https://doi.org/10.1016/J.SCITOTENV.2022.158892.
[68] M.R. Haque, M.M. Ali, W. Ahmed, M.A.B. Siddique, M.A. Akbor, M.S. Islam, M. M. Rahman, Assessment of microplastics pollution in aquatic species (fish, crab, and snail), water, and sediment from the Buriganga River, Bangladesh: an ecological risk appraisals, Sci. Total Environ. 857 (2023), 159344, https://doi.org/10.1016/J.SCITOTENV.2022.159344.
[69] F.A. Birami, B. Keshavarzi, F. Moore, R. Busquets, S.G.G. Zafarani, R. Golshani, H. Cheshmvahm, Microplastics in surface sediments of a highly urbanized wetland, Environ. Pollut. 314 (2022), 120276, https://doi.org/10.1016/J.ENVPOL.2022.120276.
[70] Y. Liu, W.Y. Jiang, Y. Liao, R. Sun, J. Hu, Z. Lu, M. Chang, J. Yang, Z. Dai, C. Zhou, P. Hong, Z.J. Qian, S. Sun, L. Ren, Y.Q. Liang, Y. Zhang, C. Li, Separation of false-positive microplastics and analysis of microplastics via a two-phase system combined with confocal Raman spectroscopy, J. Hazard Mater. 440 (2022), 129803, https://doi.org/10.1016/J.JHAZMAT.2022.129803.
[71] N. Rangel-Buitrago, R.D.B. Rodríguez, J.B. Moreno, F.L. Ochoa, W. Neal, Are sediment textural parameters an "influencer" of microplastics presence in beach environments? Mar. Pollut. Bull. 184 (2022), 114125 https://doi.org/10.1016/J.MARPOLBUL.2022.114125.
[72] C. Ding, M. Jiao, Y. Wang, Z. Yao, T. Li, W. Wang, S. Cao, R. Li, Y. Wang, Distribution and retention of microplastics in plantation mangrove forest sediments, Chemosphere 307 (2022), 136137, https://doi.org/10.1016/J.CHEMOSPHERE.2022.136137.
[73] C.A. Faseyi, M.K. Miyittah, L. Yafetto, A.A. Sowunmi, G. Lutterodt, Pollution fingerprinting of two southwestern estuaries in Ghana, Heliyon 8 (2022), e10337, https://doi.org/10.1016/J.HELIYON.2022.E10337.
[74] I. Pinho, F. Amezcua, J.M. Rivera, C. Green-Ruiz, T. de J. Piñón-Colin, F. Wakida, First report of plastic contamination in batoids: plastic ingestion by Haller's Round Ray (Urobatis halleri) in the Gulf of California, Environ. Res. 211 (2022), 113077, https://doi.org/10.1016/J.ENVRES.2022.113077.
[75] R.L. Laju, M. Jayanthi, K.I. Jeyasanta, J. Patterson, N.G.G. Asir, M.N. Sathish, J.K. P. Edward, Spatial and vertical distribution of microplastics and their ecological risk in an Indian freshwater lake ecosystem, Sci. Total Environ. 820 (2022), 153337, https://doi.org/10.1016/J.SCITOTENV.2022.153337.
[76] M. Flores-Cortés, J.S. Armstrong-Altrin, Textural characteristics and abundance of microplastics in Tecolutla beach sediments, Gulf of Mexico, Environ. Monit. Assess. 194 (2022) 752, https://doi.org/10.1007/s10661-022-10447-4.
[77] K. Gedik, A.R. Eryaşar, R.Ç. Öztürk, E. Mutlu, K. Karaoğlu, A. Şahin, Y. Özvarol, The broad-scale microplastic distribution in surface water and sediments along Northeastern Mediterranean shoreline, Sci. Total Environ. 843 (2022), 157038, https://doi.org/10.1016/J.SCITOTENV.2022.157038.
[78] E. Dhivert, N.N. Phuong, B. Mourier, C. Grosbois, J. Gasperi, Microplastic trapping in dam reservoirs driven by complex hydrosedimentary processes (Villerest Reservoir, Loire River, France), Water Res. 225 (2022), 119187, https://doi.org/10.1016/J.WATRES.2022.119187.
[79] M. Jiao, Y. Wang, T. Li, R. Li, B. Liu, Riverine microplastics derived from mulch film in Hainan Island: occurrence, source and fate, Environ. Pollut. 312 (2022), 120093, https://doi.org/10.1016/J.ENVPOL.2022.120093.
[80] P. Thamsenanupap, T. Tanee, J. Kaewsuk, Evidence of microplastics in the Chi River Basin, Thailand: anthropogenic influence and potential threats to edible arthropods, Limnologica 97 (2022), 126030, https://doi.org/10.1016/J.LIMNO.2022.126030.
[81] N. Bošković, D. Joksimović, O. Bajt, Microplastics in fish and sediments from the Montenegrin coast (Adriatic Sea): similarities in accumulation, Sci. Total Environ. 850 (2022), 158074, https://doi.org/10.1016/J.SCITOTENV.2022.158074.
[82] A. Ridall, J. Ingels, Seasonal and spatial variations in microplastics abundances in St. Andrew Bay, Florida, Sci. Total Environ. 852 (2022), 158422, https://doi.org/10.1016/J.SCITOTENV.2022.158422.
[83] I.M. Widiastuti, N. Serdiati, A.M. Tahya, Study of microplastic sediment abundance in palu bay, central sulawesi, Indonesia, Aquac. Aquarium, Conserv. Legis. 14 (2021) 2857–2865. https://www.proquest.com/scholarly-journals/study-microplastic-sediment-abundance-palu-bay/docview/2615451606/se-2?accountid=14777.
[84] D.A. Utami, L. Reuning, O. Konechnaya, J. Schwarzbauer, Microplastics as a sedimentary component in reef systems: a case study from the Java Sea, Sedimentology 68 (2021) 2270–2292, https://doi.org/10.1111/sed.12879.

[85] D. Toyama, V.V. Fernandes, A.L. Christoforo, D.B. Menezes, The artificialization in the sediment profiles of the streams in the Água Branca basin – itirapina, São Paulo, Brazil, J. Environ. Manag. 290 (2021), 112610, https://doi.org/10.1016/J.JENVMAN.2021.112610.
[86] K. Chouchene, J.C. Prata, J. da Costa, A.C. Duarte, T. Rocha-Santos, M. Ksibi, Microplastics on barra beach sediments in aveiro, Portugal, Mar. Pollut. Bull. 167 (2021), 112264, https://doi.org/10.1016/J.MARPOLBUL.2021.112264.
[87] Y. Liu, J. Di Zhang, Y. Tang, Y. He, Y.J. Li, J.A. You, F. Breider, S. Tao, W.X. Liu, Effects of anthropogenic discharge and hydraulic deposition on the distribution and accumulation of microplastics in surface sediments of a typical seagoing river: the Haihe River, J. Hazard Mater. 404 (2021), 124180, https://doi.org/10.1016/J.JHAZMAT.2020.124180.
[88] Y.S. Ibrahim, S.R. Hamzah, W.M.A.W.M. Khalik, K.M.K. Ku Yusof, S.T. Anuar, Spatiotemporal microplastic occurrence study of setiu wetland, south China sea, Sci. Total Environ. 788 (2021), 147809, https://doi.org/10.1016/J.SCITOTENV.2021.147809.
[89] V. Castelvetro, A. Corti, J. La Nasa, F. Modugno, A. Ceccarini, S. Giannarelli, V. Vinciguerra, M. Bertoldo, Polymer identification and specific analysis (PISA) of microplastic total mass in sediments of the protected marine area of the meloria shoals, Polymers 13 (2021), https://doi.org/10.3390/polym13050796.
[90] L. Portz, R.P. Manzolli, G.V. Herrera, L.L. Garcia, D.A. Villate, J.A. Ivar do Sul, Marine litter arrived: distribution and potential sources on an unpopulated atoll in the seaflower biosphere reserve, caribbean sea, Mar. Pollut. Bull. 157 (2020), 111323, https://doi.org/10.1016/J.MARPOLBUL.2020.111323.
[91] R. Li, L. Yu, M. Chai, H. Wu, X. Zhu, The distribution, characteristics and ecological risks of microplastics in the mangroves of Southern China, Sci. Total Environ. 708 (2020), 135025, https://doi.org/10.1016/J.SCITOTENV.2019.135025.
[92] O. Konechnaya, S. Lüchtrath, L. Dsikowitzky, J. Schwarzbauer, Optimized microplastic analysis based on size fractionation, density separation and μ-FTIR, Water Sci. Technol. 81 (2020) 834–844, https://doi.org/10.2166/wst.2020.173.
[93] M.A. Asadi, Y.A.P. Ritonga, D. Yona, A.M.S. Hertika, Vertical distribution of microplastics in coastal sediments of bama resort, baluran national park, Indonesia, Nat. Environ. Pollut. Technol. 18 (2019) 1169–1176. https://www.proquest.com/scholarly-journals/vertical-distribution-microplastics-coastal/docview/2327881867/se-2?accountid=14777.
[94] M.A. Asadi, A.M.S. Hertika, F. Iranawati, A.Y. Yuwandita, Microplastics in the sediment of intertidal areas of Lamongan, Indonesia, Aquac. Aquarium, Conserv. Legis. 12 (2019) 1065–1073. https://www.proquest.com/scholarly-journals/microplastics-sediment-intertidal-areas-lamongan/docview/2277978173/se-2?accountid=14777.
[95] F. Saliu, S. Montano, M.G. Garavaglia, M. Lasagni, D. Seveso, P. Galli, Microplastic and charred microplastic in the faafu atoll, Maldives, Mar. Pollut. Bull. 136 (2018) 464–471, https://doi.org/10.1016/J.MARPOLBUL.2018.09.023.
[96] M. Renzi, A. Blašković, P. Fastelli, M. Marcelli, C. Guerranti, S. Cannas, L. Barone, F. Massara, Is the microplastic selective according to the habitat? Records in amphioxus sands, Mäerl bed habitats and Cymodocea nodosa habitats, Mar. Pollut. Bull. 130 (2018) 179–183, https://doi.org/10.1016/J.MARPOLBUL.2018.03.019.
[97] M. Zobkov, E. Esiukova, Microplastics in Baltic bottom sediments: quantification procedures and first results, Mar. Pollut. Bull. 114 (2017) 724–732, https://doi.org/10.1016/J.MARPOLBUL.2016.10.060.
[98] R.L. Coppock, M. Cole, P.K. Lindeque, A.M. Queirós, T.S. Galloway, A small-scale, portable method for extracting microplastics from marine sediments, Environ. Pollut. 230 (2017) 829–837, https://doi.org/10.1016/J.ENVPOL.2017.07.017.
[99] J. Masura, J.E. Baker 1959-, G.D. (Gregory D. Foster, C. Arthur, C. Herring, Laboratory Methods for the Analysis of Microplastics in the Marine Environment : Recommendations for Quantifying Synthetic Particles in Waters and Sediments, 2015. https://repository.library.noaa.gov/view/noaa/10296.
[100] M. Kedzierski, V. Le Tilly, P. Bourseau, G. César, O. Sire, S. Bruzaud, Microplastics elutriation system: Part B: insight of the next generation, Mar. Pollut. Bull. 133 (2018) 9–17, https://doi.org/10.1016/j.marpolbul.2018.05.011.
[101] X. Zhu, Optimization of elutriation device for filtration of microplastic particles from sediment, Mar. Pollut. Bull. 92 (2015) 69–72, https://doi.org/10.1016/j.marpolbul.2014.12.054.
[102] M. Wenzel, B. Fischer, G. Renner, J. Schoettl, C. Wolf, J. Schram, T.C. Schmidt, J. Tuerk, Efficient and sustainable microplastics analysis for environmental samples using flotation for sample pre-treatment, Green Anal. Chem. 3 (2022), 100044, https://doi.org/10.1016/j.greeac.2022.100044.
[103] F. Yuan, X. Li, W. Yu, J. Du, D. Wang, X. Yang, C. Zhou, J. Wang, H. Yuan, A high-efficiency mini-hydrocyclone for microplastic separation from water via air flotation, J. Water Process Eng. 49 (2022), 103084, https://doi.org/10.1016/j.jwpe.2022.103084.
[104] M. Claessens, L. Van Cauwenberghe, M.B. Vandegehuchte, C.R. Janssen, New techniques for the detection of microplastics in sediments and field collected organisms, Mar. Pollut. Bull. 70 (2013) 227–233, https://doi.org/10.1016/j.marpolbul.2013.03.009.
[105] J.C. Prata, J.P. da Costa, A. V Girão, I. Lopes, A.C. Duarte, T. Rocha-Santos, Identifying a quick and efficient method of removing organic matter without damaging microplastic samples, Sci. Total Environ. 686 (2019) 131–139, https://doi.org/10.1016/j.scitotenv.2019.05.456.
[106] M.G.J. Löder, M. Kuczera, S. Mintenig, C. Lorenz, G. Gerdts, Focal plane array detector-based micro-Fourier-transform infrared imaging for the analysis of microplastics in environmental samples, Environ. Chem. 12 (2015) 563–581, https://doi.org/10.1071/EN14205.
[107] Y. Chen, D. Wen, J. Pei, Y. Fei, D. Ouyang, H. Zhang, Y. Luo, Identification and quantification of microplastics using Fourier-transform infrared spectroscopy: current status and future prospects, Curr. Opin. Environ. Sci. Heal. 18 (2020) 14–19, https://doi.org/10.1016/j.coesh.2020.05.004.
[108] N. Parashar, S. Hait, Occurrence and removal of microplastics in a hybrid growth sewage treatment plant from Bihar, India: a preliminary study, J. Clean. Prod. 376 (2022), 134295, https://doi.org/10.1016/J.JCLEPRO.2022.134295.
[109] J.L. Xu, K.V. Thomas, Z. Luo, A.A. Gowen, FTIR and Raman imaging for microplastics analysis: state of the art, challenges and prospects, TrAC, Trends Anal. Chem. 119 (2019), 115629, https://doi.org/10.1016/J.TRAC.2019.115629.
[110] A. Dehaut, L. Hermabessiere, G. Duflos, Microplastics detection using pyrolysis-GC/MS, in: T. Rocha-Santos, M. Costa, C. Mouneyrac (Eds.), -Based Methods BT - Handbook of Microplastics in the Environment, Springer International Publishing, Cham, 2020, pp. 1–35, https://doi.org/10.1007/978-3-030-10618-8_27-1.
[111] J. Logemann, E. Oveland, Ø. Bjorøy, wibke peters, C. Cojocariu, T. Kögel, Pyrolysis-GC-Orbitrap MS - a Powerful Analytical Tool for Identification and Quantification of Microplastics in a Biological Matrix, 2018.