Journal Pre-proof

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PII: S0045-6535(21)00827-4

DOI: https://doi.org/10.1016/j.chemosphere.2021.130357

Reference: CHEM 130357

To appear in: *ECSN*

Received Date: 22 December 2020

Revised Date: 16 March 2021

Accepted Date: 20 March 2021

Please cite this article as: Bellasi, A., Binda, G., Pozzi, A., Boldrocchi, G., Bettinetti, R., The extraction of microplastics from sediments: An OVERVIEW of existing methods and the PROPOSAL of a NEW and green alternative, *Chemosphere*, https://doi.org/10.1016/j.chemosphere.2021.130357.

Highlights

- Microplastics (MPs) contamination is an environmental issue
- Plastic particles have been observed almost worldwide in every natural environments
- A proper quantification of dispersed particles in sediments is still difficult
- Different extraction methods of MPs from sediments are described
- A valid alternative in term of reliability and costs for the extraction is proposed

THE EXTRACTION OF MICROPLASTICS FROM SEDIMENTS: AN OVERVIEW OF EXISTING METHODS AND THE PROPOSAL OF A NEW AND GREEN ALTERNATIVE

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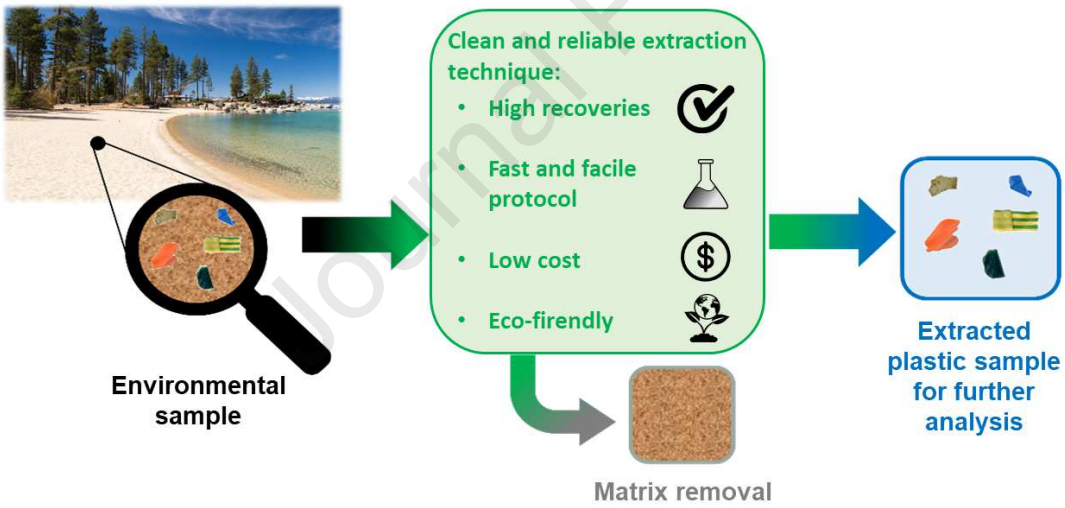
Graphical abstract



Abstract: Microplastics (MPs) contamination is an existing and concerning environmental issue. Plastic particles have been observed worldwide in every natural matrix, with water environments being the final sink of dispersed MPs. Microplastic distribution in water ecosystems varies as a function of multiple factors, including polymer properties (e.g., density and wettability) and environmental conditions (e.g., water currents and temperature). Because of the tendency of MPs to settle, sediment is known to be one of the most impacted environmental matrices. Despite the

increasing awareness of their diffusion in sediments, a proper quantification of dispersed particles is still difficult, due to the lack of standard protocols, which avoid a proper comparison of different sites. This hampers the current knowledge on environmental implications and toxicological effects of MPs in sediments. In this work, we examined 49 studies carried out from 2004 to 2020 to describe the different extraction methods applied, and to highlight pros and cons, with the aim of evaluating the more promising protocols. Therefore, we evaluated each proposed method by considering precision, reproducibility, economic viability and greenness (in term of used reagents). Finally, we proposed a valid alternative procedure in term of reliability and costs, which can attract increasing interest for future studies.

Keywords: microplastic, sediment, extraction method, standard protocol, density separation, oleophilic

1. Introduction

Microplastics (MPs, i.e. plastic particles with size <5mm) pollution in natural habitats has been considered a potential concern since 1980s [1], however only recently it has been recognized as a global threat due to its diffusion at a worldwide level [2]. Indeed, all the environmental compartments are reported to be affected by plastic pollution [3–6] and water environments are known to be the most struck [7].

MPs have been recognized as an “emerging contaminant” [8,9] due to their persistence, ubiquity and risks posed to aquatic and soil organisms [10–19]. Besides direct negative effects derived from the ingestion of particles [20–22], MPs can act as both sources of toxic chemicals by releasing plasticizers and additives [23–25], which can lead to a disruption of biological processes (eg, endocrine disruption [26,27]), and as sinks for hydrophobic contaminants [28,29]. Moreover, recent findings showed that MPs can also interact with trace metals in environmental conditions, acting as a vector for toxic element uptake by aquatic and terrestrial organisms [13,30–32].

More recently, the degradation of MPs and the further formation of nanoplastics, defined as particle smaller than <1 µm [33], have attracted considerable interests at global scale for their environmental implications. However, the technical difficulties in investigating particles of this size in the environmental media have hindered to obtain reliable comprehension of their ecotoxicological effects [34].

Whereas studies concerning the presence of MPs in waters date back to 1970s [35], only in late 1990s, scientists have started to monitor both sediment and beach litter [36–38]. The number of records available in Scopus database (https://www.scopus.com/home.uri) regarding studies that explore the presence of MPs in sediments are much less abundant than those of MPs in water (Figure 1). Moreover, research on MPs in sediments became relevant after 2010, and only from 2016 they have started to increase exponentially.

While the presence of MPs in sediments is reported worldwide [10,40,41], the lack of a standardized method of analysis hampers the complete assessment of MPs pollution in sediments [39], and therefore, still now, it is difficult to evaluate the ecotoxicological implications of MPs in this compartment [40].

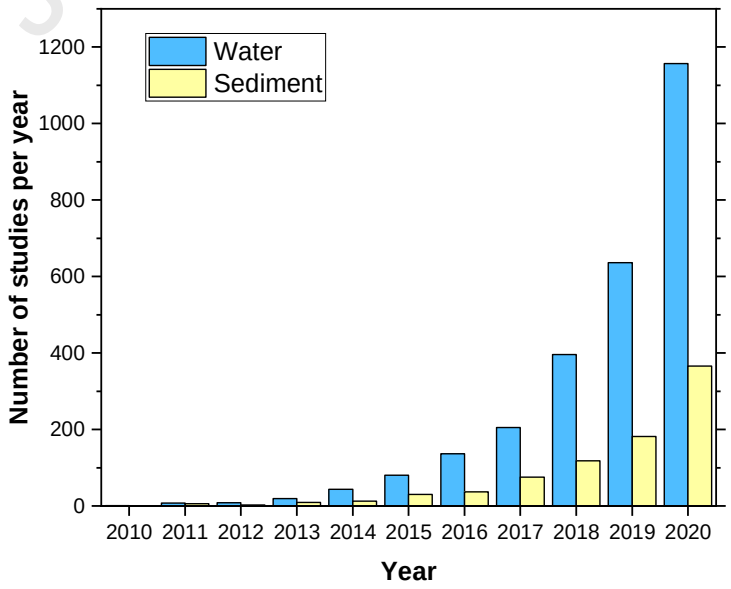


Figure 1: a comparison of studies concerning the presence of MPs in sediments (in yellow) and water compartment (in blue) from the last ten years. Data were obtained by searching "microplastics + sediments" and "microplastics + water" on Scopus database.

The fate of MPs in aquatic ecosystems, including sediments, depends on several variables related to both the water body (e.g., wind, currents, and geographical location [40]) and the plastic properties (e.g., the polymer density and the grade of ageing [42,43]). Therefore, while floating plastic litter might be easily deposed on beaches, causing severe pollution of this compartment, plastic particles sink along the water column reaching the sediment. Furthermore, due to the dynamics of MP sedimentation [44], those particles loaded with pollutants or incorporated in organic matter are more likely to sink and accumulate in sediments [45,46,47], leading to an increased accumulation of contaminants in this compartment and possibly enhancing toxicological risks for benthic organisms. The sediment compartment also shows anoxic conditions which favor the accumulation of chemicals. Indeed, the anoxic environment alters the redox equilibria, and since the load of metals is highly affected by the geochemical background [48,49], several anthropogenic metals (e.g. Pb, Cd and Hg) and hydrophobic contaminants can accumulate in higher content compared to the water column [50,51].

Consequently, there is an increasing necessity to quantify litter and characterize MP particles in sediments [52]. The first step to gain a clearer comprehension of the effects of MPs on ecological processes is to properly measure their abundance [53]. In this context, several studies have been already carried out as sediments result seriously threatened by different effects of plastic pollution [4,51,54–61]. However, despite the increasing awareness and concerns, a standard protocol to extract MPs from these compartments is still lacking [62]. The lack of a unified method hinders data harmonization and comparison in different environmental settings, making a global comprehension of the amount of plastic dispersed in sediments unrealizable.

Principal confounding factors of MP quantification in sediments are related to: i) selection of the sampling site and temporal pattern [4,52,63–67]; ii) risk of procedural contamination during laboratory protocols [68], correlated also to possible reagent contamination [69]; iii) efficiency of separation strategy; and iv) the lack of a harmonized measurement unit, which leads to an unreliable comparison of results [70]. For instance, some data are expressed as number of MPs per mass of sediments (dry or wet) [57], whereas others as items per m^2 , making the entity of contamination impossible to understand [71]. As an example, the level of MPs contamination in European rivers still cannot be compared due to this discrepancy in measurement units [40].

While wide effort has been invested in reviewing sampling procedure, little interest has focused on the chemical extraction and analytical techniques for a systematic characterization of plastics [62,72–76], as well as on the comparison of separation techniques to isolate MP samples from the matrix, which is still missing in literature. Recent reviews, in fact, overlooked the comparison of methods also in terms of costs, feasibility and sustainability of the chemicals adopted for extraction [77–80]. Therefore, considering the general lack of knowledge, in this paper, we described different methods of MPs extraction from sediments, considering also pros and cons. The aim of this study is to support the development of a standardized protocol to allow not only data comparison, but also a complete understanding of the entity of contamination in sediments by MPs. Finally, this study also proposed an alternative, reproducible, green and cost-effective method for density separation.

2. Reviewed Literature

A total of 49 studies, carried out in different locations from 2004 to 2020, was collected and compared to evaluate the whole development of the extraction techniques, starting from the first deployed one up to the most recently proposed. Studies concerning MPs contamination in sediments are much more than 49 (see Figure 1), but often provided information are redundant and unclear. Our intention was to consider different case studies carried out with several approaches

without providing too much information with the aim to avoid gaining a confused and fragmentary understanding.

Although this study is mainly focused on MPs in lacustrine sediments, we decided to include also research carried out on aquatic sediments in general, to avoid the disregard of some worthy methods.

Across all studies considered, 73.5% (N = 36) research [4,8,61,64,81–88,10,89–98,53,99–104,54–57,59,60] used methods based on density separation, 10.2% (N = 5) used a density separation combined with other techniques [105–108], and 6.1% (N = 3) used oil extraction strategy [109–111]. The remaining studies employed elutriation [112] and electrostatic separation techniques [113], as well as depolymerization and subsequent quantification methods of terephthalic acid [114,115]. In few cases, different analytical protocols were proposed in combination [114].

From Table 1, it is possible to note that different discrepancies between the considered methods still exist. Besides the measurement units, also the size range of separated MPs is not consistent in the available literature, which is possibly due to the lack of a univocal definition of MPs [105]. However, the size of particles is a key factor in establishing the extraction potentials [94] and this parameter needs to be considered for the selection of the separation method to deploy. In addition, quality assurance and quality control (QA/QC) factors are not always expressly illustrated by each authors and, since contamination of samples is an important source of error, this aspect should be taken into account as this could influence the results obtained by each applied method [116].

Bearing in mind these weaknesses, different extraction protocols are fully analyzed in the next paragraphs, with a particular focus on density separation method, which represents the most applied technique in literature so far (Table 1).

Table 1: Summary of different methods proposed in reviewed studies for the extraction of MPs from sediments. Principal parameters consider to characterize each study are: (i) method: approach apply by each author; (ii) chemicals: different reagents employed in protocols; (iii) matrix: type of sediment subjected to separation process; (iv) recovery efficiency: capacity of the protocol to separate MPs from sediments; (v) unit: measurement unit used to express the concentration of MPs in sediments; (vi) size range: dimension of considered plastic particles; (vii) quality assurance and quality control factors (QA/QC): approach used during separation process with the aim to reduce and quantify sample contamination and results goodness; (viii) country: place where studies have been carried out. Some fields are incomplete due to the lack of information in studies, highlighting different approaches applied by authors.

METHOD	CHEMICALS	MATRIX	RECOVERY EFFICIENCY	UNIT	SIZE RANGE	QA/QC	COUNTRY	REFERENCE
density separation	NaCl	sediments from beaches and estuarine and subtidal sediments	-	items/mL	20 µm in diameter	-	United Kingdom	Thompson et al., 2004
density separation	NaCl	beach sediments	-	-	> 1.6 µm	-	Singapore	Ng and Obbard, 2006
density separation	NaCl	coastal sediments	-	items/mL	500 µm - 7 mm	-	Sweden	Nor, 2007

density separation	Na□WO□	beach sediments	-	-	1.38 - 6.50 mm	stainless equipment	Hawaii	Corcoran et al., 2009
density separation	filtered seawater	beach sediments	-	items/g	2 - 20 mm	-	Brasil	Ivar do Sul et al., 2009
density separation	tap water	beach sediments	-	number of particles	2-5 mm	stainless equipment	China	Zurcher, 2009
density separation	NaCl	sediments from an estuarine area	-	items/50 mL	< 1 mm	-	United Kingdom	Browne et al., 2010
density separation	NaCl	sediments from shoreline	-	-	< 1 mm	cotton clothing	Australia, Japan, Oman, United Arab Emirates, Chile, Philippines, Azores, South Africa, Mozambique, UK	Browne et al., 2011

density separation	NaCl	sediments from shoreline	-	mean % abundance	250 µm - 4 mm	-	Hawaii	Carson et al., 2011
density separation	NaCl	marine sediments	68.8% - 97.5%	items/kg d.w.; mg/kg d.w.	-	-	Belgium	Claessens et al., 2011
density separation	NaCl	beach sediments	-	items/m²	50 µm - 5 mm	plasticfree equipment	Portugal	Martins and Sobral, 2011
density separation	ZnCl□	aquatic sediments	95.5 ± 1.8	-	< 1 mm - 5 mm	plasticfree equipment	Germany	Imhof et al., 2012
density separation	ZnCl□	beach sediments	-	items/10 g d.w.	< 100 µm	triplicate analyses	Frisian Islands	Liebezeit and Dubaish, 2012
elutriation + density separation	NaI	spiked sediments	100% PVC, 98% fibers, 94%-98% microspheres	-	10 µm - 250 µm	-	-	Claessens et al., 2013
density separation	ZnCl□	beach sediments	95.5%	abundance %	< 500 µm - < 5	-	Lombardy, Lake	Imhof et al., 2013

					cm		Garda	
elutriation + density separation	NaI	beach sediments	-	items/L; kg/d.w.	-	-	Belgium	Van Cauwenbergh e et al., 2013a
density separation	NaCl	sediments from shallow areas	-	items/kg d.w.	15 µm - 2.5 mm	plasticfree equipment, cotton laboratory coats, procedural blanks	Venice	Vianello et al., 2013
density separation	water	beach sediments	-	g/L	< 5 mm	-	Canary Islands	Batzan et al., 2014
density separation	NaCl	beach sediments	-	items/ g d.w.	< 5 mm	-	Canada	Mathalon et al., 2014
fluidization + density separation	(i) NaCl; (ii) NaI	beach sediments	99% ± 3.0 PE; 96% ± 6.6 PP; 97% ± 6.4 PVC; 91% ± 10.4 PET; 92% ± 9.8 PS; 68% ± 24.8 EPS; 96% ± 9.2	number of particles	500 µm - 3 mm	stainless equipment	Frisian Islands	Nuelle et al., 2014

			PUR					
fluidization + density separation	(i) NaCl; (ii) NaI	beach sediments	-	items/kg d.w.	500 µm < x < few cm	plastic free equipment, procedural blanks	Frisian Islands	Dekiff et al., 2014
density separation	CaCl□	beach sediments	0-40% yellow, orange and pink particles; 45% - 63% transparent particles; 60%-100% blue, violet and green particles (PE)	items/kg d.w.	< 1.5 mm	plastic free equipment, minimising the number of handling steps	Baltic coast	Stolte et al., 2015
elutriation	water	beach sediments	50.2%	-	5 mm	-	-	Zhu et al., 2015
density separation	NaCl	shoreline sediments	-	items/kg d.w.	< 300 µm - 1	stainless equipment	central Italy	Fischer et al., 2016

					mm		(Lake Chiusi, Lake Bolsena)	
oil extraction protocol	canola oil	shoreline sediments	96.1% ± 7.4	%/kg	> 400 µm	stainless equipment	Canada	Crichton et al., 2017
density separation	ZnCl□	estuarine sediments	95.8% ± 1.6	items/kg d.w.	100 µm - 1 mm	cleaned equipment placed inside a laminar flow hood and covered with clean aluminium foil	United Kingdom	Coppock et al., 2017
density separation	ZnCl□	river sediments	-	items/10 g	1 - 4 mm	control samples	United Kingdom	Horton et al., 2017
density separation	NaCl	canal and marine sediments	-	items/kg d.w.	10 µm - 5 mm	plastic free equipment; procedural blanks	Holland	Leslie et al., 2017
density separation	tap water - NaCl - NaBr - NaI - ZnBr□	marine sediments	200-400 µm - H□O 85-95%; NaCl ±90%; NaBr >90%; NaI ± 95%; ZnBr□ ±	-	200 µm - 1 mm	cotton laboratory coats, plastic free equipment, cleaned equipment, taping technique to examine lab benches, control of atmospheric contamination, procedural blanks	Scotland	Quinn et al., 2017

			95%; 800-1000µm - H□O 60-80%; NaCl 70-80%;NaBr > 80%; NaI ± 90%; ZnBr□ >95%					
density separation	Food-grade table NaCl – reagent grade NaCl	sand	HDPE - reagent grade NaCl: 81.28%-95.11%; food-grade table NaCl 36.99%-74.42	µg/kg	100 - 850 µm	plastic free and cleaned equipment, cotton laboratory clothes	Spain	Sánchez-Nieva et al., 2017

two step density separation	ZnCl□	bottom marine sediments	92 ± 7%	items/kg d.w.	> 400 µm	cotton aboratory clothes, plastic free equipment, evaluation of air dispersed MPs	Baltic Sea	Zobkov et al., 2017
electrostatic separation	Korona Walzen Scheider	quartz sand, freshwater sediments, beach sand	100%	-	63 µm - 5 mm	-	-	Felsing et al., 2018
two step density separation	NaCl	river sediments	-	items/kg d.w.	20 µm - 5 mm	procedural blanks, cotton laboratory clothes, plastic free equipment	China	Lin et al., 2018
centrifuged with salt solution – density separation	CaCl□	marine sediments	-	items/kg d.w.	100 µm - 5 mm	-	Canada	Collicutt et al., 2019
density separation	KF	river sediments	-	items/kg d.w.	< 100 µm - > 1mm	-	China	Fan et al., 2019
density separation	mix NaCl-NaI	soil and sediments	90%	items/kg d.w.	100 µm - 6 mm	-	China	Han et al., 2019
density separation	NaCl	strandline sediments	86% - 90%	items/kg d.w.	< 1 mm - 5 mm	plastic free equipment	Slovenia	Korez et al., 2019

oil extraction protocol	castor oil	marine beach sediments	spiked sample: 99% ± 4.4; environmental sample: 74% ± 13	-	300 µm - 1mm	plastic free equipment	-	Mani et al., 2019
density separation	NaCl	stream sediments	-	items/kg d.w.	500 µm - 2mm	plastic free equipment, procedural blanks	Tunisia	Toumi et al., 2019
density separation	NaI	surface and core sediments	-	items/kg d.w.	50 µm - 5mm	filtration of all epmployed liquids, plastic free equipment, cotton laboratory clothes, procedural blanks	China	Wang et al., 2019
PET depolymerization and quantification of the terephthalic acid (TPA) monomer	Dichloromethane, diethyl ether, xylene, methanol, hydrogen peroxide, sulfuric acid, acetic acid, sodium hydroxide, hexadecyl-	marine and freshwater sediments	98.2%	ppb	-	preliminary evaluation of exhaustiveness of the recovery of TPA	Italy	Castelvetro et al., 2020

	tributyl-phosphonium-bromide, zinc acetate, deuterated chloroform, hexafluoroisopropanol							
combination of different analytical protocols	-	freshwater sediments	-	ppm	< 2mm	-	Italy	Corti et al., 2020
oil extraction protocol	canola oil	river sediments	67% ± 2.3 (fibres); 63% ± 3.5 (microbeads); 61% ± 2.2 (fragments)	items/kg d.w.	< 400 µm	laminar flow hood, plastic free and cleaned equipment, cotton laboratory clothes, procedural and contamination blanks	Canada	Crew et al., 2020
PET depolymerization and	methanol, butanol, hydrochloric	beach sediments	94.5% - 107.1%	mg/kg	-	-	Germany	Müller et al., 2020

quantification of the terephthalic acid (TPA) monomer	acid, potassium hydroxide							
density separation	(i) NaCl; (ii) $ZnCl_2$	beach and bed marine sediments	> 85%	recoveries %	-	plastic free equipment, cotton laboratory clothes, control blanks, all water used during procedures was filtered. All steps were carried out inside a flow cabine	Portugal	Rivoira et al., 2020
density separation	ZnCl□	organic rich sediments	90.7% ± 7.7	items/L	100 µm-3 mm	plastic free equipment, cotton laboratory clothes, procedural blanks	Japan	Vermeiren et al., 2020
heating assisted density separation	NaH□PO□	beach sediments	93%	items/kg d.w.	100 µm-5 mm	plastic free equipment	China	X. Zhang et al., 2020
density separation	NaCl - KI	deep-sea sediments	-	items/kg d.w.	100 µm-5 mm	plastic free equipment, cotton laboratory clothes, procedural blanks	western Pacific Ocean	D. Zhang et al., 2020
two step density separation	NaCl	river sediments	-	items/kg d.w.	300 µm-5 mm	cotton laboratory clothes, evaluation of atmospheric MPs, procedural blanks	China	L. Zhang et al., 2020

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3. Proposed methods for extraction of MPs

The separation of MPs from complex matrices is a laborious practice that can represent an important source of error in the MPs quantification [117]. The content of organic matter in sediments is affected by the environmental conditions of deposition: in lentic ecosystems, where the decomposition rate is high, the quantity of organic matter found in sediments results higher than that in riverine ecosystems [118]. A good estimate of the organic content and the application of an adequate digestive process are key steps for an efficient separation of plastic particles [119]. Indeed, the main factor that affects results is the tendency of confusing the plastic particles with residual natural debris and organic matter. Furthermore, automatized techniques for this process are still not reported, so the extraction protocol may take long times. Therefore, finding an efficient and easy applicable protocol would maximize the success of the process. In the following paragraphs, we report the principal methods proposed in literature for MP extraction.

3.1. Density separation

Density separation is a method based on differences in densities between sediments and MPs [111]. The separation between sediments (with an average density of 2.65 g/cm^3 [21,120]) and MPs (which are less dense, with a maximum density of 1.58 g/cm^3, Table 2) is achieved by producing a fixed density solution for the separation, mixing filtered or distilled water with a variable amount of a selected salt. In this way, while sediments particles settle down, MP particles float on the superficial layer of the dense solution [111,121] and can be easily separated to undergo further analysis. In this process, the selection of the density of the extraction solution in relation to that of the polymer type is crucial [122]. Therefore, the different densities of plastics and those of the extraction solutions reported in literature are summarized in Table 2 and 3, respectively.

Density separation to extract MPs from sediment matrix is the most used technique [123], representing 73% of considered studies (Table 1). Although this method appears to be easily applicable, a careful choice of the most appropriate salt is required to achieve the right density of

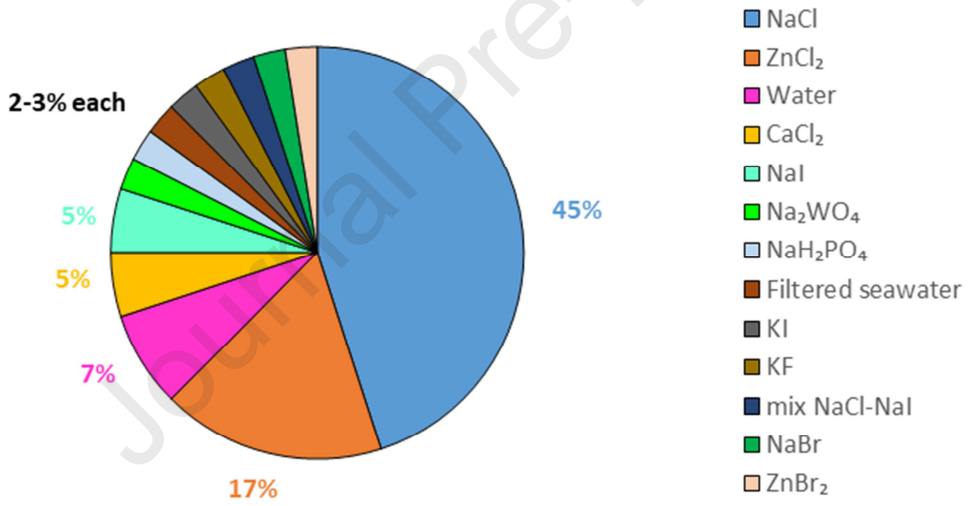
the solution and the best recovery rate of plastic. Moreover, during the density separation process, organic matter may float with plastic particles, making complicated to discriminate plastic litter from organic matter and, therefore, the method might require further treatments (e.g., chemical digestion [102,[125]).

Table 2: Densities of the principal types of plastic polymers [126]

Polymer	**Density (g/cm^3)**
polyethylene (PE)	0.917 - 0.965
polypropylene (PP)	0.9 - 0.91
polystyrene (PS)	1.04 - 1.1
Nylon	1.02 - 1.05
Polyester	1.24 - 2.3
polyvinylchloride (PVC)	1.16 - 1.58
polyethylene terephtalate (PET)	1.37 - 1.45
Polyurethane	1.2

Sodium chloride (NaCl) is the most used salt to perform density separation, representing 45% of studies from literature (Figure 2). The choice of NaCl is principally related to the fact that this

169 salt is low cost and "environmentally friendly" [66,122]. However, some polymers (principally
170 polyester, PVC and PET) have a higher density than NaCl (1.2 g/cm^3) and, therefore, can not be
171 separated using this approach [111]. In order to increase the recovery rate of MPs, some authors
172 have tested other higher density salts, such as zinc chloride ($ZnCl_2$) [53,55,57,88,101,122], sodium
173 iodide (NaI) [60,122], calcium chloride ($CaCl_2$) [92], sodium tungstate (Na_2WO_4) [82],
174 monosodium phosphate (NaH_2PO_4) [102], sodium bromide (NaBr) [94], zinc bromide ($ZnBr_2$) [94],
175 potassium iodide (KI) [61] and potassium fluoride (KF) [98]. In a recent study from 2019, Han et al.
176 [99] proposed a mix between NaCl and NaI to increase the recovery rate of MPs, reaching a density
177 of 1.5 g/cm^3. Differently, some other authors tried to perform density separation by using tap water
178 [83,90,94,127] or filtered seawater [54].



179

180 **Figure 2:** Chemicals used to perform density separation in considered studies.

181 The various alternative of chemicals for density extraction procedure led to confusion in choice
182 of the most suitable method. To clarify the most suitable salts for density separation, a comparison
183 of the main physicochemical characteristics of the different salts proposed in literature is reported in
184 Table 3, considering also the sustainable and economic aspects.

185 From a density prospective, since polymer vary from 0.9 (PP) to 1.58 (PVC) g/cm^3 in density,
186 $ZnCl_2$, NaI, KI, $ZnBr_2$ and KF are considered the best salts to achieve an efficient density

separation. Howecer, while these substances provide better performances of extraction [122], they have the drawback to be dangerous for aquatic biotas (Table 3) [111] and present serious health hazards; zinc chloride, for instance, can be corrosive. Moreover, NaI, Na□WO□, KI and KF are expensive, so they may not be suitable to achieve MPs extraction using large amount of sample or for long monitoring programs.

Alternatively, NaH□PO□ appears to be a good compromise: it allows reliable extraction performances, it is cost-effective, non-hazardous, and able to achieve a good recovery rate [102]. However, the extraction with NaH□PO□ could be overly complex due to the necessity to heat the solution to enhance its density, possibly decreasing method replicability. $CaCl_2$ represents another good alternative due to the low cost and relatively low risks, but this compound has a density ranging between 1.3 and 1.35, which does not allow the retention of PET (1.37 – 1.45) and PVC (1.16 – 1.58) particles. For this reason, $CaCl_2$ density should be incremented for extraction procedure.

To the best of our knowledge, $ZnCl_2$ has emerged as the most performing density separation method in terms of both recovery [53,55,87,101] and process simplicity. However, $ZnCl_2$ is very expensive, and therefore should be used for a second density separation after a NaCl step, [104]. Morever, it is an hazardous substances, and thus, its use should be avoided.

Once the most appropriate salt has been selected, some attention should be given to develop a relevant procedure protocol to perfom the MPs analyses, as well to the glassware and materials to be used. In this context, some authors have based their density separation protocol on only one extraction [8,10,81], whereas some others performed a second extraction to achieved the best separation rate [57,60,85,86,89,101]. Since several studies have recommended the necessity to repeat flotation duplicating the process could be a good strategy to optimize results [57,105]. With regard to materials to use, authors usually achieve a satisfying separation by using laboratory glassware [8,56,86,89]; however, in some other cases, special devices such as Munich Plastic Sediment Separator (MPSS) [87], Sediment-Microplastic isolation unit (SMI) [53], and a separation

column with a top overflow (OC-T) [101] have been developed. In general, the use of canonical glassware would be advantegeous as this, compared to special devices, does not force the physic separation of plastic particles from sediments. Moreover, the use of standard glassware combined with an appropriate extraction solution have already prooved to achieve an easy and feasible MP analyses.

Table 3: Characteristics of substances used to achieve density separation in considered literature. Different colors are used to highlight the quality of each features (green for good, orange for average and red for poor). Data on chemicals characteristics are retrieved from ECHA database (European Chemicals Agency, https://echa.europa.eu/information-on-chemicals), while prices are from Sigma-Aldrich (www.sigmaaldrich.com)

SUBSTANCE	FINAL DENSITY OF SOLUTION (g/cm^3)	CAS no.	HAZARD CLASSIFICATION	PRICE (€/kg)
Sodium chloride	1.2	7647-14-5	No hazards have been classified	107.00 (reagent grade) 0.45 - 3.00 (table grade)
Zinc chloride	1.5 - 1.8	7646-85-7	Severe skin burns and eye damage; very toxic to aquatic life with long lasting effects; harmful if swallowed	137.00
Sodium iodide	1.8	7681-82-5	Damage to organs through prolonged or repeated exposure; very toxic to	574.00

			aquatic life; causes serious eye irritation and skin irritation	
Calcium chloride	1.3 - 1.35	10043-52-4	Causes serious eye irritation	81.20
Sodium tungstate	1.4	10213-10-2	Harmful if swallowed	504.00
Monosidum phosphate	1.4 - 1.45 (40°C)	7558-80-7	No notified hazards by manufacturers, importers, or downstream users	91.10
Potassium iodide	1.7	7681-11-0	Damage to organs through prolonged or repeated exposure. Additionally, the classification provided by companies to ECHA in CLP notifications identifies that this substance is toxic to aquatic life with long lasting effects, may damage fertility or the unborn child, causes serious eye and skin irritation, is harmful if swallowed, may cause an ellergic skin reaction, may cause allergy or asthma symptoms or breathing difficulties if inhaled and may cause respiratory irritation.	306.00
Sodium bromide	1.37	7647-15-6	No hazards have been classified	138.60
Zinc bromide	1.7	7699-45-8	Severe skin burns and eye damage,	195.00

			toxic to aquatic life with long lasting effects, harmful if swallowed, may cause allergic skin reactions	
Potassium fluoride	1.5	7789-23-3	Toxic if swallowed, toxic in contact with skin, and toxic if inhaled	316.00

After a proper extraction, floating particles can be separated from the flotation medium using different procedures. The most common one is generally performed by filtering the superficial layer [8,81,87] or by adding a dense solution in excess to overflow supernatant [57,95]. Other complementary processes can be applied after the extraction procedure, which includes elutriation or centrifugation, both allowing to reduce possible sample loss, and therefore increasinge the recovery rates [105,107,108]. Collicutt et al. [106], for instance, have applied a method to extract MPs that combines the use of a $CaCl_2$ saturated solution with centrifugation; other authors performed a MPs extraction by preceding floatation in a saturated NaI solution with an elutriation step, with the aim to decrease the sediment sample mass and improve the separation [108]. Elutriation process can be also applied as a separate method [127]: it consists in an upward stream of gas or liquid by which ligther particles are separated from heavier ones.

3.2. Oil extration protocol (OEP)

The extraction of MPs from sediments using oil is an innovative method based on the oleophilic properties of plastics. This method is independent from the plastic density characteristics and is unaffected by the presence of organic matter in samples, which

differently floats together with MPs, when density separation is applied. Furthermore, this process presents high cost-effectiveness and easiness of application [107–109].

The oil extraction protocol (OEP) was firstly proposed by Crichton et al. [111] and later revisited by other authors [107,108]. Practically, the protocol consists in adding few milliliters of oil to the filtered water mixed with dry sediments, and then, placing the solution in a shaker, to allow the oil to get in contact with the sample; these steps are followed by a funnel extraction. At this point, the oil layer is filtered, and then filters are treated with reagent (e.g., alcohol or no-foaming detergent) to remove the oil residues that could affect subsequent analysis.

One of the procedural errors that all protocols need to face is derived from the possibility that particles might remain in sediments without dispersing in oil [109,111] or remain on filters when manually collected [108], leading to an underestimation of MP abundance. Despite these limitations, Crichton et al. [111] and Mani et al. [110] reported good recovery rates on spiked sediment samples, but those rates decreased when tested on a real environmental sample [109].

Potential weaknesses have been identified from this first proposed method, that consist principally in the incompatibility of the detergent and reagent alcohol with the Raman and FTIR analysis, and in the underestimation of coarser particles of extracted MPs, due to the outlets size of the separation funnel used in the protocol [129]. Further studies tried to adjust several steps of this method to improve the overall performances. For instance, Scopetani et al. [128] resolved these weaknesses by promoting separation in polytetrafluoroethylene cylinders equipped with a removable cap and a piston, when

dealing with MPs in soil and compost. Following this protocol, samples are frozen at -40°C and only the oil layer is pushed out and filtered. Filters are subsequently rinsed with hexane, rather than reagent alcohol, to avoid interferences with spectroscopic methods [111], and polymer particles are collected to undergo further analysis.

Overall, OEP is an efficient method that allow to overcome problems related to density and costs of reagents. From the available literature, generally authors used 3 mL to a maximum of 10 mL [110] of oil for each extraction, and, considering treating 50 g of sediments at time, with 1 L of oil is possible to achieve separation of 5 kg and 17 kg of sediments, respectively.

Besides oil, the use of detergents, alcohol [111] or hexane [109] is needed to clean filters and, therefore, to characterize polymers by spectroscopic analysis. This cleaning step implies that possible sample contamination could additionally arise, even if performed directly on filtration unit [111]. Moreover, the use of other substances increases costs and the environmental hazard of the method. To avoid the use of additional reagents, Mani et al. [110] proposed to pick separated particles by hand to perform chemical analysis by FTIR, however, this alternative could easily cause the loss of particles, leading to underestimation.

In summary, research effort is still needed to optimize the protocol and to reduce the number of steps involved to reduce possible source of errors and sample contamination.

3.3. Other proposed methods

In addition to the use of density separation and OEP, Felsing et al. [113] performed electrostatic separation to achieve MP separation from sediments , other authors tried to pressurize fluid extraction [130], others used depolymerization and subsequent quantification of terephthalic acid [114,115], and Corti et al. a combination of different analytical protocols [131]. All the mentioned procedures showed notable results, with relatively fast separations, however, they are seldom used since they require complex instrumentation settings. The following paragraphs described in details the abovementioned procedures.

3.3.1. Electrostatic separation

The electrostatic separation [125] permits to separate plastic particles from the matrix, basing on their electrostatic properties [113].

In the first study reporting this methodology [113], the authors used a Korona-Walzen-Scheider (KWS) separator, manufactured by Hamos GmbH (Penzberg, Germany). In this process, the sample is inserted in the system by a filling funnel and then the particles are scattered onto the metal drum by the vibrating conveyer. By rotating, metal drum brings particles into a high-voltage field where the electrostatic charging of particles takes place. Due to the rotational movement of the drum, the particles are discarded into different sample collectors according to their speed of discharge: non-conductive materials (MPs) are slower than conductive materials (sands grains) and so are collected in separate discharged zones.

Felsing et al. [113] obtained a separation efficiency as high as nearly 100%, demonstrating the effectiveness of this method. Electrostatic separation allows to overcome issues of density and possible alteration of MPs structure caused by chemicals [108]. Moreover, both sample handling and number of procedural steps are reduced, increasing method replicability. However, a separator device could be very expensive and unprofitable to analyze small amounts of sediments, and this is the reason why the use of this method is still limited.

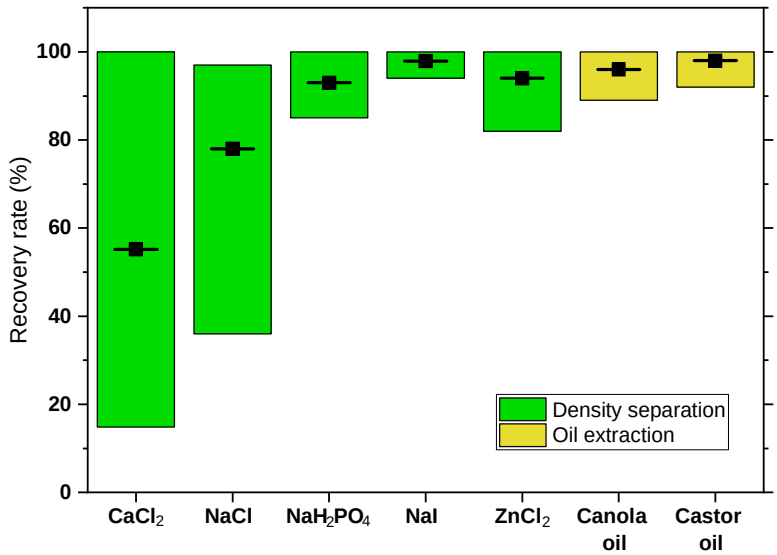
3.3.2. Pet depolymerization and quantification of terephthalic acid

This method has been proposed with the aim to quantify PET micro and nanoparticles using an accurate and sensitive protocol [114,115]. It consists of an aqueous alkaline depolymerization of PET with a phase transfer catalysis, followed by an HPLC quantification of terephthalic acid (TPA), which is assumed to be the only dicarboxylic acid comonomer in this polymer. The alkaline depolymerization of PET results in the formation of 1:1 mixture of TPA salt and ethylene glycol, then, by quantifying TPA, it is possible to derive the amount of PET in the sample.

The TPA quantification can be affected by interference with other organic compounds, however the recovery rate is up > 94% [114,115]. Limitations of this process are several: first only PET can be analyzed, secondly, samples are destroyed, making further investigations unavailable. Finally, this procedure involves the use of several chemicals to perform the reactions and requires expensive equipment.

4. Comparison of proposed methods

From the comparison of the described techniques, it emerges that recovery efficiency shows a wide variance (Figure 3), even when the same method is applied. In the case of density separation, the salt selected to perform the separation not only can lead to differences in recovery rates, but also to high variance [53,101]. This may depend on variability in the procedures used by each author, and from the density of extracted plastic particles, which, overall, highlights the urgent need to develop a standard procedure protocol. Another issue that might influence the extraction rates is related to the polymer particles size range. As highlighted in a study carried out by Quinn et al. [94], same reagents show different efficiency based on the target MP sizes. However, the whole considered density separation methods shown a recovery efficiency > 80%, except for separations performed with food-grade table NaCl [95] and $CaCl_2$ [92]. In fact, Stolte et al. [92] revealed the efficiency rate for two samples which are 49% and 62% respectively, with an average value of 55,5%.



337 **Figure 3:** Comparison of recovery rates reachable on spiked sediments using density
338 separations with different salts, and with oil extraction procedures on spiked sediments.
339 Red and yellow areas indicate the ranges, while black symbols indicate the average values.
340 Data for $CaCl_2$ are from Stolte et al., 2015 [92]; data for NaCl are from Claessens et al., 2011
341 [85], Korez et al., 2019 [59], Sanchez-nieva et al., 2017 [95]; data for NaH_2PO_4 from Zhang et
342 al., 2020 [102]; data for NaI from Claessens et al. 2013 [105]; data for $ZnCl_2$ from Vermeiren
343 et al., 2020 [101], Coppock et al., 2017 [53]; data for canola oil from Crichton et al., 2017
344 [111]; data for castor oil from mani et al., 2019 [110]; data for olive oil from Scopetani et al.,
345 2020 [128]. Only studies reporting recovery rates are depicted, and, regarding density
346 separation, only the most used salts.

347 Furthermore, a general trend observed in literature showed lower recovery values in
348 real environmental samples compared with spiked ones. This fact is evident in the study
349 carried out by Mani et al. [110]. Authors reported a recovery rate of 99% ± 4.4% on spiked
350 sediments, while only 74% ± 13% of MPs extracted from environmental samples. This
351 discrepancy might be related to the high heterogeneity in shape, size and color of
352 environmental plastic debris compared with laboratory-prepared plastic particles used for
353 spiking, making both the visual inspection and quantification after extraction more
354 complicated. The relation between the extraction efficiency and the particles aspect is
355 highlighted by Stolte et al. [92]. In this study, yellow, orange and pink particles are
356 recovered with an efficiency ranging from 0 to 40%, whereas blue, violet, and green
357 particles from 60% to 100%. The inefficient recovery of some particles may depend on the
358 difficulties related to visual identification carried out by the operator [132]. Moreover, the

visual discrimination of plastic particles gets also particularly problematic when organic matter and sediment grains are not completely removed.

In summary, relevant characteristics that need to be considered when selecting the most promising protocol for future studies include precision, reproducibility, and costs of the extraction method in relation to the targeted MPs. On this regard, all methods are summarized in table 4, considering also their suitability.

Table 4: Suitability of proposed methods. +: favorable; ±: medium; -: unfavorable

METHOD	PRECISION	REPRODUCIBILITY	COST
Density separation	±	+	±
Oil extraction protocol	±	+	+
Electrostatic separation	+	+	-
Chemical extraction	±	±	-

According to the parameter established in table 4 and the recovery rates showed in table 1, the electrostatic separation appears to be the most efficient method, but not for routinely plastic extraction, due to high costs and complexity of process. On the contrary, both the density separation and OEP are suitable techniques for routinely analysis. A more detailed comparison of these methods is reported in figure 3, which addresses the most suitable extraction [53,59,85,87,92,95,99,101,102,109–111,128].

372 Although the number of recovery efficiency rates reported for OEP is lower than that
373 for density separation, data appear to be more homogeneous (Figure 3). Overall, recovery
374 rates for both density separation and OEP are mainly above 80%, with exception for $CaCl_2$
375 and NaCl, which show high variance of extraction recoveries. In summary, although some
376 aspects need to be further addressed to improve their recovery efficiency and replicability, these
377 procedures are easily reproducible and cost effective.

378 **5. An environmentally friendly alternative**

379 To reach a suitable and green method to extract MPs from sediments, we propose a density
380 separation using a mixture of NaCl and sucrose. This method is based on a low cost, widely used
381 and environmental friendly reagent for separation in biological field [133,134].

382 *5.1. Preliminary evidence*

383 As previously reported, a NaCl saturated solution has the limit of being not dense enough to
384 efficiently separate all type of plastic particles, however, by mixing NaCl with sucrose, it is possible
385 to increase its density. In figure 4 the experimental relation between the percentage of added
386 sucrose (Carlo Erba reagents, RPE grade) and the density of the NaCl saturated solution is reported.
387 These measurements have been produced after laboratory procedures carried out at the University
388 of Insubria.

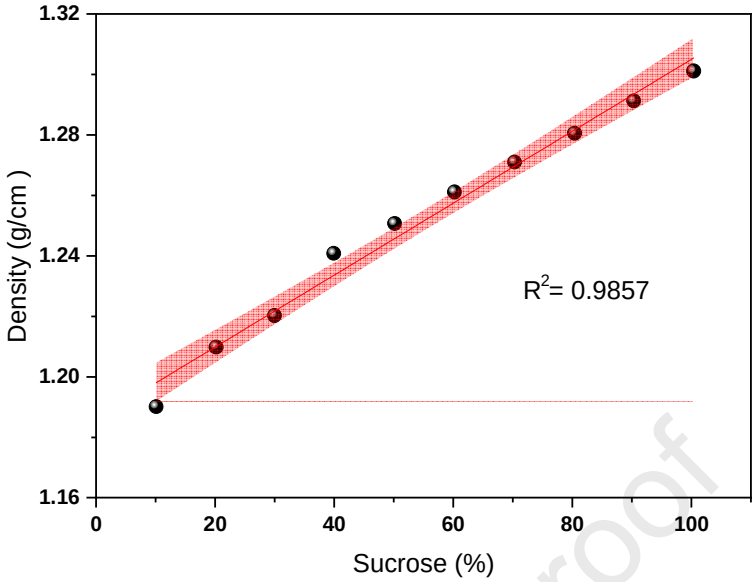


Figure 4: Relation between % (weight/volume) of added sucrose and density of NaCl saturated solution. Black dashed line indicates the regression line and light blue area indicate the 95% confidence interval.

Using a saturated NaCl solution (prepared with ultrapure water) with an addition of 100% (weight/volume) sucrose, a density of approximately 1.30 g/cm^3 was achieved. To prepare this solution, small amounts of sucrose were added to the saturated solution on a magnetic stirrer equipped with a hot plate. The solution was heated at 50°C to accelerate the dissolution of sucrose.

MPs, with size range of 500 µm to 3 mm, were produced by mechanical fragmentation of larger items. We selected polymers of this size range to test this method because larger MPs are easily detectable; moreover, the use of these particles contributed to identify possible method weaknesses related to the viscosity of the solution. In this light, 10 MP particles for each type were insert in different beakers, then NaCl/sucrose solution was added, and beakers were vigorously shaken to verify if plastic particles would sink or float on solution surface. Laboratory tests were carried out in triplicate.

Mean flotation percentage values for each polymer are provided in figure 5, while data about flotation results in table S1.

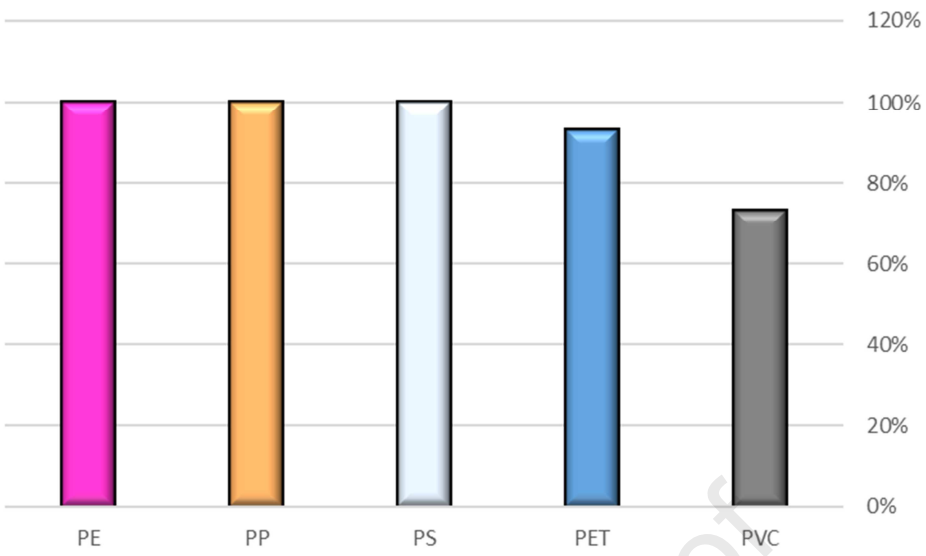


Figure 5: Mean flotation % for each polymer basing on 3 flotation tests. On y-axis % mean flotation is reported.

PS (1.04 – 1.1 g/cm^3), PE (0.917 – 0.965 g/cm^3), and PP (0.91 g/cm^3) responded to the treatment according to their densities, reaching a mean flotation of 100%, whereas heavier PET (1.37 – 1.45 g/cm^3) and PVC (1.58 g/cm^3) reached a mean flotation of 93.30% and 73.30%, respectively.

It should be noted that some high-density polymers (e.g., PVC) can be partially recovered even if the density of the solution is theoretically not supposed to separate all types of plastics. Indeed, besides the density factor, the viscosity of the solution could influence particles separation as well. In the current study, the viscosity of the sucrose solution has been calculated based on the equation proposed by Galmarini et al. [135]:

$$viscosity = A_0\, e^{(A_1 * c)}$$

where A_0 and A_1 are empirical parameters (at 20°C: A_0 = 0.586; A_1 = 0.059) and c is the concentration expressed as g of sucrose/100g. Assuming that NaCl does not promote the increasing of the solution viscosity, the viscosity of the present sucrose solution is about 213 mPa.

5.2 Evaluation of recovery efficiency on spiked sediments

Since preliminary tests highlighted the possibility to theoretically achieve a complete separation not only of lighter particles (PE, PP, PS) but also of heavier polymers, such as PVC and PET, we tested this method on spiked sediments.

To evaluate the separation efficiency, 3 aliquots of 50 g d.w. sediments were put in 3 different glass beakers and spiked with a known number of MPs produced in laboratory by mechanical degradation. After the addition of MPs, sediments were put in a separation funnel. NaCl/sucrose solution was added in 3:1 ratio (150 mL of solution for 50 g d.w. sediments) and then the separation funnel was vigorously shaken. After completed sedimentation, spiked sediments were separated from the solution, that was directly collected into a Büchner funnel for filtration. Sediments were rinsed 3 times, and the recovered MPs were collected on cellulose filters and then, visual sorted using a stereoscope to assess the separation efficiency. This separation process was tested in 4 replicates, and the recovery rates achieved in each test are shown in table S2.

More than half of spiked MPs were separated in each test, with a mean %R.R of approximately 82.5%. As expected, PP and PE showed a recovery rate ranging from 90% to 100%, while PS, a recovery rate slightly lower than the other light polymers. This is possibly related to the shape of PS fragments, which enhance the trapping in sediments grains, or to the white color of PS. Indeed, this coloration pose difficulties during visual sorting as filters are white as well. The addition of sucrose to a NaCl saturated solutions allowed also to partially recover heavier polymers such as PET (mean R.R. 73,3%) and PVC (mean R.R. 53,3%).

Considering the results presented here, the addition of sucrose could be a good environmentally friendly strategy to improve NaCl saturated solution density, and, thus, to avoid the use of dangerous chemicals. However, although the promising preliminary results, this method needs to be further developed and validated to overcome procedural obstacles related to both MPs sizes and stickiness of solution, that could promote particles adhesion on vessels surfaces.

5.3. QA/QC procedures

To avoid possible sample contamination and the consequent associated errors in estimating the efficiency of the method, laboratory tests were carried out in quadruplicate and procedural blanks were used for each separation test. During the separation process, a glass beaker filled with NaCl/sucrose solution was kept on the workstation to evaluate the potential contamination of the handled sample. Moreover, to avoid contamination with air dispersed fibers, cotton laboratory clothes were used, and work position was kept clean all time. Plastic free equipment was used and was accurately rinsed with distilled water before each use. When possible, a flow cabine was used.

6. Conclusions

In summary, this review highlights a complete lack of a harmonized process for the monitoring of MPs in sediments from the available literature. By considering precision, reproducibility, greenness, and costs of each described method, the most suitable approach appears to be the oil extraction protocol. Oils are, indeed, quite cost-effective, and the extraction requires a small amount of oil to be performed [110,128]. The precision of the method depends on the accuracy by which each step is carried out, and, therefore, could be increased by developing a pre-treatment protocol. In fact, the interference with natural matrix in environmental samples represents a factor highly affecting results [110], as showed in spiked samples, with a recovery rates > 90% [110,111].

Despite the suitability of OEP, density separation remains the most applied technique. This method has the advantage of easiness in experimental setup as it does not require any specific instrumentation and lacks complex operations. Furthermore, this method is a non-destructive technique, which allows to characterize samples also after the quantification procedure. Nonetheless, a density separation method which results safe and, at the same time, efficient is still not present in literature. Therefore, a procedure that increases density without employing harmful substances is still needed.

In this context, the use the sucrose density gradient technique proposed here might represent an innovative green solution, that would allow to separate heavier polymers, as supported by our

preliminary findings. Moreover, besides provide a good strategy to separate plastic particles in a safe way, NaCl/sucrose solution is economically competitive. Considering using 1 kg of sucrose and about 260 g of NaCl in 1 L of deionized water and to recycle solution adjusting density after filtration, investing about 15.00 € is possible to perform separation on about 100 g d.w. sediments. However, although the reported performances are good for the 500 µm -3 mm size range, the extraction strategy needs to be investigated with smaller particles, and a method needs to be complete developed to overcome practical obstacles during the process (e.g., the collection of plastic particles in the viscous solution). Despite these general considerations, the aspect related to the identification techniques need to be further developed. Indeed, apart from the method choice, if the separated material needs to be filtered, it is important that filter is not too crowded in order to perform a successful characterization [91].

After the disentangling of different pros and cons of extraction methods to contribute to the development of a harmonized extraction protocol, the future perspectives in MP analysis in sediments include:

1. the application of green, fast and reliable extraction methods in real samples and their test on field scale (e.g. long-time trends or regional monitoring programs);
2. inter-laboratory tests for the creation of harmonized standard protocols [132];
3. nanoplastics extractions from sediments, which showes more critical aspects for analytical protocols;
4. a standardized quantification systems (e.g. measurement units) to better compare studies in different areas worldwide and better quantify plastic pollution.

Author Contributions: A. Bellasi, G. Binda, R. Bettinetti conceptualization; A. Bellasi formal analysis; A. Bellasi writing-original draft; G. Binda, A. Bellasi data curation; G. Binda, A. Pozzi, R. Bettinetti, G. Boldrocchi writing-review and editing; R. Bettinetti supervision. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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Declaration of interests

☒ 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.

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