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Misidentification of PVC microplastics in marine environmental samples

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A B S T R A C T

Poly(vinylchloride), PVC, is the third most demanded polymer in Europe although its presence in marine ecosystems, surprisingly, is scarcely observed. This does not reflect neither its production nor its widespread usage. Therefore, it is imperative to understand why this may happen. PVC is the least stable of the high-tonnage produced polymers as it has the highest sensitivity towards UV radiation and, therefore, photo-degradation is of maximum relevance. The big amount of additives included in PVC formulations, weathering and the different treatments required to isolate it from environmental samples can modify the surface of PVC microplastics, making their spectral identification/quantification an analytical challenge. All these factors can lead to large PVC underestimations in environmental studies, in which other polymers like PE, PP or PS outstand. Further, the fact that the infrared spectrum of weathered PVC can be confounded with that of PE is of most relevance and, therefore, remarkable misidentifications and/or wrong quantifications may occur. In this work some relevant factors that can explain the low percentages of PVC reported in the literature are discussed and special emphasis is made on the need for suitable spectroscopic databases that include PVC weathered standards. This has been confirmed by the results of a detailed study of PVC weathering under pilot-scale conditions, monitoring its spectroscopic and physical changes over time.

1. Introduction

The incorrect management of petroleum-based plastic waste has led to the accumulation of huge amounts of plastics in the environment, especially in the marine ecosystem, often the final sink for most plastic residues [1]. It was estimated that between 4 and 12 million tonnes of plastic enter the World's oceans annually, primarily from coastal inputs [2].

There are more than 5000 types of synthetic polymers but ca. 80% of the total plastic items are from polypropylene (PP), polyethylene (PE), poly(vinylchloride) (PVC), poly(ethyleneterephthalate) (PET) and polystyrene (PS) [3]. PVC is the third most demanded polymer in Europe, and so the third in production after PP and PE [4], and contribute 19% of global plastic production [5]. It is a thermoplastic, i.e. it can melt when heated and hardened when cooled. These characteristics are reversible and, therefore, it can be reheated, reshaped and cooled repeatedly [4]. The manufacture of PVC can be schematized as composed of four major stages: i) generation of ethene from cracking of ethane, propane or petroleum naphthas; ii) chlorination of ethene to get 1,2-dichloroethane; iii) subsequent pyrolytic cracking to obtain the monomer (chloroethene or vinyl chloride); and iv) PVC results from the addition polymerisation of vinyl chloride monomers. Typical suspensions of polymerised PVC have a mean particle size of 100–150 μm with a 50–250 μm range. The particles are complex and irregular in shape with a dense semipermeable surface (Patrick, 2004). PVC commercial products are based on the combination of the polymer resine plus additives that render the formulation necessary for the end-use requirements.

The unique polar characteristics of PVC permit a wide range of additives to be incorporated within it and, in fact, additives amount to percentages within the PVC resins [6]. Hence, PVC formulations can include many different types of additives to assist producers in obtaining a range of physical and chemical characteristics suitable for each application. In general, thermal and UV stabilizers are added to extend the lifetime and stability of PVC products that are exposed to sunlight whereas plasticizers or flexibilizers (as phthalates, lead compounds, organotin compounds, etc.) are added

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to improve flexibility. This versatility is the main reason why PVC has become so successful as a commodity thermoplastic: medical applications, such as tubing and blood bags; clothing fabric; long-life applications, such as window frames and waterproof goods; industrial applications (pipes, cables, etc), or in food packing [5,7], to mention but some examples. In spite of the thermal, UV stabilizers or biocides added to PVC, it was seen that PVC microplastics (MPs) that stayed in marine environments for a long time became highly degraded [8].

The abundant production and applications of PVC are, curiously, not reflected usually in the results gathered from microplastics (MPs) environmental pollution studies. There, polymers like PE, PP or PS dominate the reports related to the marine environment worldwide. Indeed, PVC is not detected or only scarcely reported in very low abundance percentages ($\approx$1–2%). Therefore, it is imperative to understand why this may happen and, likely, to propose accurate working approaches to positively identify PVC particles avoiding their misidentification [3]. A reason that explains its usual lack of detection may be, for example, that the exposition of PVC particles to a wide variety of marine physical, chemical and biological conditions alter the original polymer composition, at least, at their surface. Hence, the identification of weathered PVC by infrared (IR) spectrometry (the commonest analytical technique) is cumbersome and hardly leads to correct assignments due to the spectral changes the polymer underwent and the usual lack of reference weathered spectra for matching [9]. Other possible explanations may be the different protocols for sampling, extraction, identification and characterization used in MPs analysis, all of them critical steps for the successful identification of plastics in the environment.

The aims of this work are threefold: to study the weathering processes of PVC in the marine environment and to evaluate how they can affect PVC identification; to scrutinize the measurement process to identify causes of PVC misidentification in environmental studies, and to eventually propose solutions to assess more closely the real quantity of PVC in environmental matrices. To achieve these latter objectives an exhaustive literature review of the most recent publications whose main interest was on identifying MPs was done.

2. Methods

2.1. Instrumentation

A 400 FT-IR PerkinElmer Spectrometer (4000-650 cm^{-1}, 4 cm^{-1} nominal resolution, Beer-Norton strong apodization, 50 scans per spectrum, background-, depth-penetration- and baseline-correction) equipped with a horizontal one-bounce attenuated total reflectance (ATR) diamond crystal (Miracle ATR, Pike) and a FTIR-microscopy (Spotlight 200i, PerkinElmer) was employed throughout. Commercial databases and an ad-hoc polymer library were used for the identification and comparison of polymer particles.

Scanning electron microscopy (SEM) was employed to characterize further the weathering process. First, the particles were manually placed over an electrically conductive, non porous carbon type (Agar Scientific, UK). Then, their surfaces were coated with a layer of gold using a cathodic spraying system (BAL-TEC SCD 004) and, then, analysed in a JEOL JSM 6400 device, under standard conditions.

2.2. Accelerated artificial weathering conditions

The PVC employed in this study was fabricated by Vinnolit Gmbh (Germany, product Vinnolit S3268) with a particle size distribution around 80 μm (range 20–130 μm) and it was prepared under the framework of the JPI-Oceans' Baseman project. It was manufactured with the lowest possible amount of additives.

A pilot-scale weathering system developed to simulate ageing under marine conditions at the Earth's medium latitudes was used [10]. Briefly, pristine PVC MPs were immersed in sea water and exposed to constant irradiation using two metal halide lamps (UV/VIS radiation, ca. 350 nm until ca. 800 nm. ca. 12200 lux illuminance, 24 $\mu W/cm^2$) during 10 weeks. Temperature in the water (as measured with a 0–100 °C range glass thermometer) was on average 25 °C, with a 23–28 °C variation range. The system contained sea-sand and was kept agitated constantly by air-pumps (AC9908 Resun Air Pump, 20 L/min).

Moreover, PVC weathering under dry conditions (to mimic the upper shoreline conditions) was assessed as well by exposing 10 g of PVC powder to the radiation in 12 cm diameter Petri dishes (without seawater, and without continuous agitation). The content of each Petri dish was mixed every day and the locations of the dishes were interchanged each three days.

Aliquots of these setups were withdrawn each fortnight to monitor weathering. More specific details are presented elsewhere [10].

3. PVC weathering

A first point to consider when reflecting on the lack of PVC identification is that, usually, weathered plastics collected from the marine environment show considerable physical and chemical differences to pristine ones [11]. This is particularly so for PVC as it has the highest sensitivity towards UV radiation among commonest plastics and, therefore, photo-degradation is of utmost importance for it. When exposed to sunlight its dechlorination is the first step, which leads to the formation of conjugated double bonds in a polyene polymer and hydrogen chloride [8].

The IR spectra of pristine and weathered PVC (after 10 weeks of simulated marine weathering) are compared in Fig. 1. As expected, they differ significantly. Two new bands are clearly visualized: at $\approx$1600 cm^{-1}, which indicates the formation of conjugated double bonds (C=C stretching), and the typical broad band at $\approx$ 3000 cm^{-1} (O–H stretching, indicative of the presence of –OH groups). Noteworthy, the spectrum of weathered PVC resembles very well the spectrum of weathered PE (Fig. 2) as PVC dechlorination derives in a polyolefin. Ketones, carboxylic acids, and carbon double bonds are the three major functional groups that appear after further photodegradation of polyethylene. Therefore, these chemical changes contribute to the misidentification of weathered PVC microplastics.

PVC weathering can be monitored by means of some spectral indices, that are calculated as ratios among selected bands of the IR spectrum [12–14]. In this work, the hydroxyl and C=C (double bonds) indexes were calculated as the ratio of the hydroxyl (3300-3400 cm^{-1}) and carbon double bonds (1600-1680 cm^{-1}) bands to a reference peak (C–H stretching band, 2900 cm^{-1}). It can be seen (Fig. 3) that both indexes increase throughout all the weathering time although faster during the last three weeks. In addition, three SEM images of artificially weathered particles of PVC are displayed. They show that the surfaces of the MPs contain small wrinkles and cracks, not seen for pristine particles. It is also observed that crystalline formations develop at the surface of the particles due to seawater salts.

The IR spectra for dry-weathered PVC revealed the same patterns as the study above, although the process seems much slower. The evolution of the two spectral indices was much smaller, by a factor of ca. 15 (C=C index) and ca. 22 (OH index). This strongly suggests that the marine environment leads to an accelerated weathering of PVC microplastics when compared to shoreline conditions.

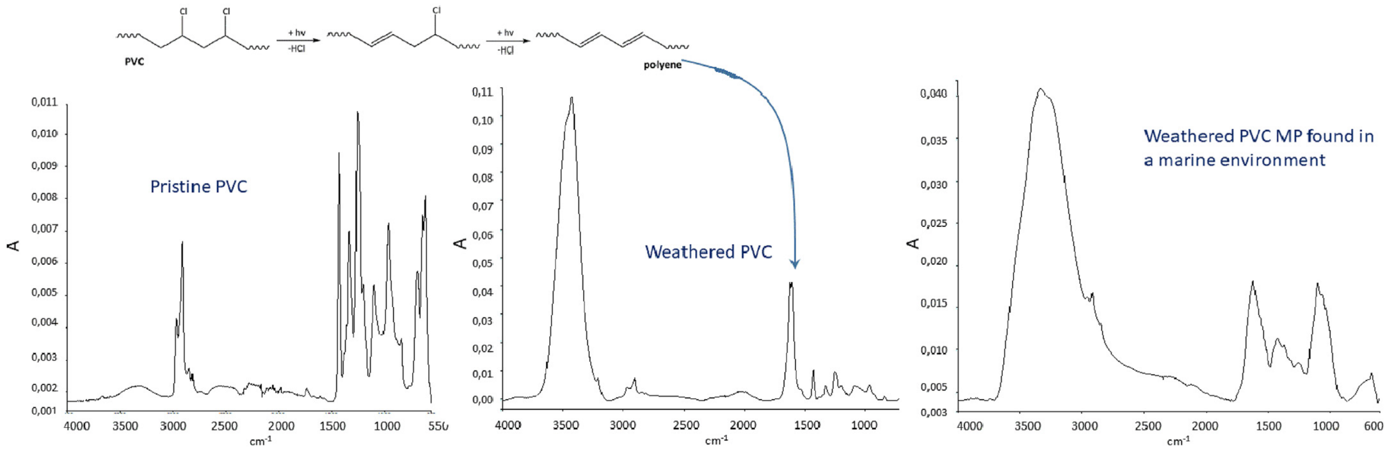

Fig. 1. FTIR spectra of pristine and weathered PVC to show the impact of its photodegradation.

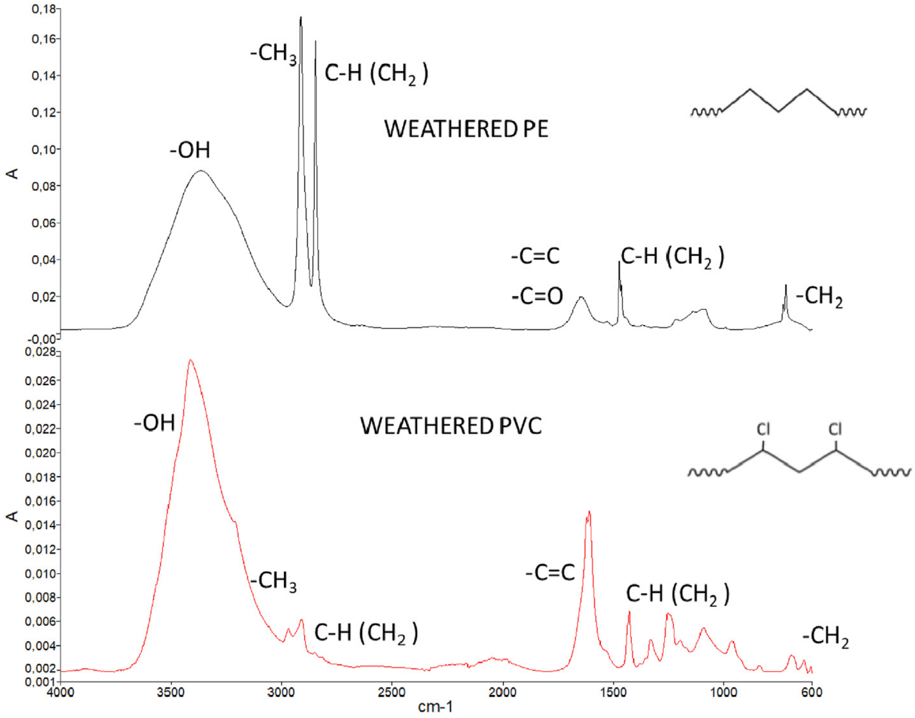

Fig. 2. Comparison of FTIR spectra of weathered PVC and weathered PE.

These results agree with the well-known fact that polymer degradation evolves through two main mechanisms: hydrolysis and (photo)oxidation. The former is defined as the interaction with water so that water molecules lead to cleavage of chemical bonds within a polymer. Photooxidation involves radical reactions (e.g. Norris I and II reactions) by which oxygen enters the polymer chain after cleavage of C═C bonds. These processes are highly potentiated by UV light as it induces formation of oxygen radical species [15,16]. Thus, it is expected that the combination of both weathering processes may lead to larger and faster polymer degradation [13,17].

A remarkable conclusion from those discussions is that unless weathered PVC spectra are included in the IR libraries used currently for polymer matching, substantial misidentification/underestimation of PVC microplastics can occur. In fact, although a match score ≥70% is commonly considered satisfactory when comparing unknown IR spectra against polymer libraries, that value is very difficult to achieve with weathered MPs [18]. As an example, environmentally-weathered PVC microplastics measured by our research group were unidentified when using current polymer IR databases implemented in the analytical system; however, they got 89% match scores when PVC particles were compared to our customized database that included weathered polymers.

This issue has also been reported in other studies where the authors hypothesized that unidentified particles could be MPs whose spectra do not match pure materials due to degradation of the constituent polymers, underlying the need for specific spectral libraries including degraded polymers [19]. So, unless this problem is addressed many reports might be skewed and lead to wrong conclusions and fault decision-making. To illustrate this, Fig. 4 compares the spectra of a pristine PVC (fabricated with reduced amounts of additives), a commercial PVC with additives and a real

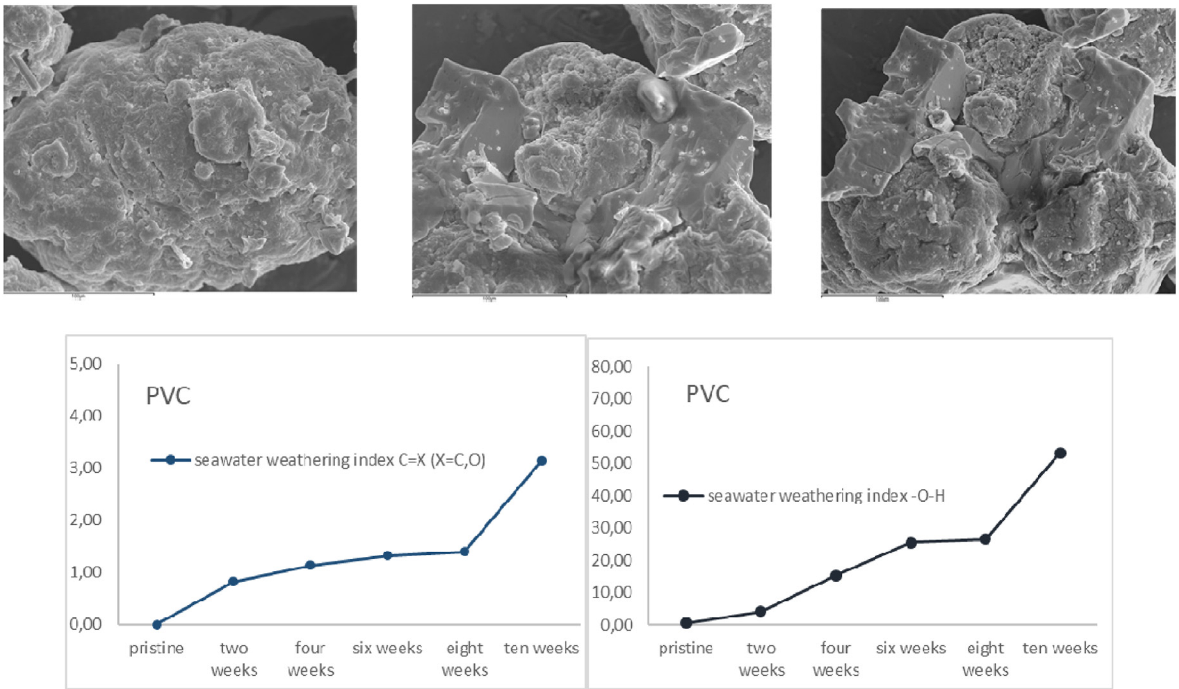

Fig. 3. Representation of two typical IR indexes employed to monitor polymer weathering, in this case PVC: C=C and OH bond indexes, and SEM images of weathered PVC particles.

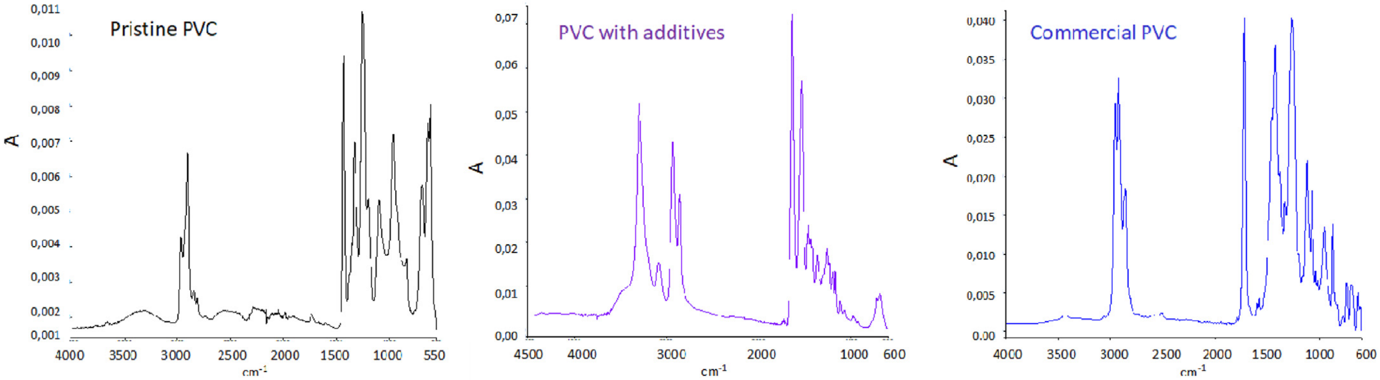

Fig. 4. FTIR spectra of a pristine PVC, a commercial PVC containing additives, and an environmentally-weathered PVC.

weathered PVC MP found in the marine environment. Observe that they three are indeed different, mainly at the fingerprint region (1500-600 cm^{-1}), with quite different profiles and relative intensities and in the CH stretching region (2800-3100 cm^{-1}), also very affected by the presence of additives. Recall that additives are not chemically bound to the PVC polymer and they can leach out, volatilize or be degraded [8], making the IR spectra different from the “original” PVC.

In order to evaluate the hypothesis we are proposing in this work to explain the frequent misidentification of PVC, a literature review of recent studies reporting on its abundance in the marine environment is presented in Table 1. Due to the huge amount of publications dealing with MPs in the marine environment, only the last three years (2018–2020) have been considered. The Web of Science database was used and the key words ‘microplastic’ and ‘environment’ were considered. The query yielded 1396 articles, of which only those that detailed the analytical procedure to determine MPs in various matrices of the marine ecosystem and that identified/differentiated the MPs according to the type of polymer were considered for this work. In total, 53 works accomplished those criteria and are reviewed here. As a matter of fact, in Table 1 only 51% of the reviewed works report the presence of PVC in their samples, and out of them, 67% report abundances below 5% for PVC (most of them below 1%). One study out of 53 indicated the use of weathered spectra to identify MPs (thanks to a collaboration within the Baseman project with our research group) [20]. Almost all other studies employed current databases to identify the MPs in the aquatic environment.

4. Analytical approaches

4.1. Analytical protocols

A second source of PVC misidentification may lie in the analytical protocols used to isolate and identify microplastics from the environmental matrices. The papers reviewed in Table 1

Table 1

Schematic resume of the reviewed publications dealing with the determination of MPs in the marine environment, providing that they identified/differentiated the constitutive polymers of the suspicious particles. The Greek letter μ denotes microscopic FTIR or Raman measurements. Microscope refers to optical microscopy, otherwise stated.

Sample matrix	Microplastics Size	Extraction/purification method	Density separation	Identification technique	Polymers found	PVC abundance	Library comparison	Reference
Seawater from Surabaya, Indonesia	from <300 μm to 5 mm	Filtration, H_2O_2 30% treatment at 80 °C 24–48 h	–	Microscope + ATR-FTIR reflection mode	PS (58.4%), PE (18.41%), PP (18.8%), PU (0.66%), PET (1.13%) polybutadiene (0.15%) and Polyester (2.39%)	Not found	–	[31]
Beach sediments from Tamil Nadu, India	from 0.5 to 3 mm	150 ml H_2O_2 30%	$ZnCl_2$	Microscope + hot needle test + ATR-FTIR	PE (73.2%), PP (13.8%), nylon (8.2%), PS (2.8%) polyester (2%)	Not found	compared with reference spectra	[32]
River waters and sediments	63 μm - 4 mm	–	$ZnCl_2$	Microscope + ATR-FTIR (30 particles out of 1507; >250 μm)	PE (50%) **PVC** (30%) PMMA (20%)	30%	Commercial polymer libraries	[5]
Beach sediments from N.W. Mediterranean Sea	63 μm – 5 mm	–	NaCl	Microscope + Fragments by FTIR + Fibers by μFTIR	Fibers: polyester, acrylic and polyacrylamide. Fragments: PP (17%), PE (15%), PS (9%) Films: PP (37%) PE (18%) PS (10%) Foam: PS (74%)	Not found	Self-collected spectrum database	[33]
Surface sediments from the S.E. Mediterranean Spanish coast	500 μm - 5 mm	–	NaCl	Microscope + μ-FTIR	PS (50%), PA (15%), PMMA (25%)	Not found	Commercial libraries and customised spectra of common weathered polymers	[20]
Sea water at Mediterranean Sea	0.33–5 mm	Samples containing high quantities of organic matter were subsequently oxidized with 3–4 ml of 30% H_2O_2 and dried in the oven at 60 °C for 12 h		Microscope + μRaman (18% of collected pieces)	PE (54.5%), PP (16.5%), PS (9.7%), and other polymers (nylon, PUR, PET, EVA, **PVC**, ABS and fluorocarbon polymers) (5.5%)	<1%	Commercial data base	[34]
Floating and seabed macro and micro litter at the Adriatic Sea	0.5–5 mm	Collected material stored in 60% ethanol	NaCl	Microscope + ATR-FTIR	PE (66.6%), PP (19.7%). EVA (2.6%) and <1% of synthetic rubbers, PMMA, PS, **PVC** and PET	«1%	Commercial libraries and a customized one	[35]
Sediments from water streams of Tunisia	0.2–5 mm	–	NaCl	Microscope + ATR-FTIR	PP and PE	Not found	Expert judgement and literature	[36]
Water column and digestive tracts of small pelagic fish from the Gulf of Lions	0.10–5 mm	–	–	Visual sorting + ATR-FTIR	Water column: PET (61%) PA (31%), **PVC** (5%), PP (2%) and PAN (2%). Digestive tracts: PET (71%), PE (18%), PA (6%) and PP (6%)	5%	Commercial libraries	[37]
Sediments and benthic organism from the Yellow Sea, China	0.05–5 mm although FTIR was used for 1–2 mm	Organism: 30% H_2O_2 and 65% HNO_3 (1:3 v/v) for two days. Then dry at 60 °C	NaI (sediments)	Microscope + FTIR	PP (31%), PE (24%), nylon (19%), PS (15%), PET (6.5%)	Not found	Commercial polymer data base	[38]
Seawater and sediments from Jiaozhou Bay, China	0.10–4 mm	Sediments dried at 50 °C for 16 h	$ZnCl_2$	Microscope + ATR-μ-FTIR	Seawater: PET (56.25%), PP (34.38%). PE (3.13%), PA (3.13%) and PVAC (3.11%) Sediments: PET (51.35%), PP (21.62%), PE (8.11%), PA (5.41%), cellophane (5.41%), **PVC** (2.7%), PS (2.7%). LDPE (2.7%)	2.7% (sediments)	Commercial library	[39]
Sediments, Norway	>250 - 10 μm	Dried in an oven at 40 °C, enzymatic digestion with protease and 30% H_2O_2. Finally, density separation	$ZnCl_2$	Pyr-GC-MS (plastics >250 μm were manually picked)	PE (32.3–139.2 μg/kg), **PVC** (9.0–120 μg/kg), PET (12–136.5 μg/kg), PS, PP, PA, PMMA, PC	9.0 –120 μg/kg	–	[40]
Waters from Kingston Harbour	Between 0.25 and 5 mm	Dried in an oven at 90 °C for 24 h, the organic material was oxidized with 0.05 M Fe(II) and 30% H_2O_2 at 75 °C	NaCl	Microscope + FTIR	PE (78%) and PP (22%)	Not found	Commercial spectral library	[41]

(*continued on next page*)

Table 1 (*continued*)

Sample matrix	Microplastics Size	Extraction/purification method	Density separation	Identification technique	Polymers found	PVC abundance	Library comparison	Reference
Sub-surface water and fish samples from the Arctic	0.5–5 mm	Gastrointestinal tract of fish: alkaline digestion (NaOH)	–	Microscope + ATR-FTIR	Water samples: PE (41.2%), PP (23.5%), **PVC** (11.8%), and <6% of PS, Ethylene-vinyl acetate, polyurethane and polyamide. Fish samples: polyester (34%), acrylic (24%), PA (21%), PE (17%), EVA (7%)	11.8% (water samples)	Commercial reference spectra libraries	[42]
Beach sand from Lanzarote, Spain	1–5 mm	–	–	Microscope + ATR-FTIR for larger particles and µRaman for the smaller ones	PE (63%), PP (32%), PS (3%)	Not found	Customized library with pure polymers	[43]
Beach sand from India	36 µm–5 mm	Coloured microplastics treated with H_2O_2	$CaCl_2$ (density 1.34 g/ml)	Fluorescence microscopy (Nile red dye) + ATR-FTIR	PE (43%), PET (17.3%), PS (17%), PP (12.3%), others (most of them polyesters and polyamides) (11%), **PVC** (1.33%)	1.33%	Polymer reference library	[44]
Beaches and water from Sri Lanka	0.1–5 mm	–	NaCl	Raman (to 20% of the particles) and ATR-FTIR (to assess level of surface oxidation)	PP, PE, PS	Not found	–	[45]
Sediments from French Atlantic coast	20–1000 µm	20 ml of demineralized water and centrifugation	Demineralized water	µ-FTIR directly on the filter	PP (38%) and PE (24%) PS (9%), **PVC** (9%) polyester (7%)	9%	Commercial polymer database	[7]
Coastal waters from Ascension and Falkland islands	<5 mm	H_2O_2 (30%) overnight	–	Microscope visual sorting and FTIR (a subset of microplastics)	PE, PET, nylon, polyester, PMMA, PS	–	–	[46]
Seawater fish and oysters from Maowei Sea, China	<5 mm	Gastrointestinal tract and gills of fish and soft tissue of oysters digested with 10% KOH, 40 °C, 48–96 h	–	Microscope and µ-FTIR	Water: Polyester, PE, PP Fish: rayon, polyester, PP Oysters: rayon, polyester	Not found	Commercial polymer library	[47]
Seawater from the N.W. Pacific Ocean	0.3–5 mm	0.05 M Fe(II) + 30% H_2O_2 and heated at 75 °C	NaCl	Microscope + µRaman	PE (58%) PP (36%) PA (3%), **PVC**, PS, rubber and PET	«3%	Reference spectra of known plastics	[48]
Offshore sediment from Yellow Sea, China	60–5000 µm	30% H_2O_2 and dried at 70 °C	NaI	Microscope + µFTIR	Cellophane (37.2%) PET (21.6%), PE (17.6%), polyester (11.8%), acrylic (9.8%)	Not found	Commercial polymer library	[49]
Water samples of Pearl River and Pearl River estuary, China	50 µm–5 mm	30% H_2O_2 room temperature and at dark for 24 h	–	Microscope + µRaman	PA (26.2%), cellophane (23.1%), PP (13.1%) PE (10%), vinyl acetate copolymers (VAC) and **PVC**	Very few items	Spectral libraries of instrument	[50]
Water from urban creeks and coastal waters from Shanghai, China	20–5000 µm	KOH (10%)	–	Microscope + ATR- µ-FTIR (285 particles out of 887)	Polyester (27.7%), rayon (14.4%), PP (8.7%)	–	Commercial database	[51]
Beach sand and mangrove sediments from China	0.16–5 mm	30% H_2O_2 (before analysing)	$CaCl_2$ + sodium metaphosphate	Optical magnifier (x10) + ATR-FTIR	PS, PE and PP	Not found	Commercial standard database	[52]
Surface sediments from urban areas at Changsha, China	0.5–5 mm	Digested with 30% H_2O_2 and Fe (II).	$ZnCl_2$	Microscope + µRaman	PS (29.41%), PE (19.12%), PET (14.71%), PP, PA and **PVC** (few particles)	Few particles	Commercial polymer library and Raman library	[53]
Surface waters from the Sea of Marmara, Turkey	0.8–65 mm	32% H_2O_2	–	Microscope + ATR-FTIR	PE, **PVC**, PP, PS	–	Confirmed with DSC measurements	[54]
Surface water of Urban Lakes in Changsha, China	0.5–5 mm	30% H_2O_2 with Fe (II) solution		Microscope + µRaman	PP (33.75%), PE (27.5%), PS (13.75), PET (11.25%), PA (7.5%) and **PVC** (3.75%)	3.75%	–	[55]
Surface waters and sediments from Pearl River, China	0.02–5 mm	Surface waters: H_2O_2 30% Sediments: KOH 10%	NaCl	Microscope + µ-FTIR	Waters: PP (35.7%), PE (28.6%), PET (28.6%), others (7.1%) Sediments: PE (47.6%), PP (26.2%)	–	Commercial database	[56]
			–	Microscope + µ-Raman		2.3%		[57]

Water column at Baltic Sea	Median size: 0.95 mm	H_2O_2 with Fenton's reagent, and digestion with HCl solution to dissolve chitin fractions			PET (25%), PA (9.1%), PE (9.1%), PP (9.1%), PS (4.5%), **PVC** (2.3%), PMMA (2.3%) and phenolic (PF) (4.5%) and polyterpene resins (PTR) (2.3%)		Commercial libraries of polymers and literature	
Water and sediments from Boahi Sea, China	<100 & >5000	Water: H_2O_2 30%	Dispersion with sodium hexameta-phosphate and flotation with NaCl. A second separation with $ZnCl_2$	Microscope + µ-FTIR	PP, PE, **PVC**, PS, PET, ABS	–	–	[58]
Water from the river shore in Mongolia	From megaplastics (>100 mm) to microplastics <5 mm	H_2O_2 30%	–	Microscope + µ-FTIR	PE and PS	Not found	Literature data	[59]
Adriatic sea water	Microplastics $\leq$5 mm	H_2O_2 60 °C	–	Microscope + ATR-FTIR (7% of total particles)	PE (66.5%), PP (17.9%). PS (4.2%), PA + polyacrylonitrile (PAN) and nylon (1.6%) PET (1%), **PVC** (0.2%)	0.2%	Instrument's and built-in libraries	[60]
Water samples of Changjiang Estuary, China	60–5000 µm	30% H_2O_2 at 60 °C	–	Suspected particles measured by ATR-µ-FTIR	PE, PP, PET, PA, styrene acrylonitrile, PS, **PVC**, PC, PU, polyvinyl alcohol, acrylate styrene acrylonitrile and acrylonitrilen butadiene styrene	–	Commercial database	[61]
Water, seafloor and beaches of China	0.5–5 mm	H_2O_2 and 0.05 mol L^{-1} $FeSO_4$ solution		µ-FTIR	Floating debris MP: PE (31.2%), nylon (22.3%), **PVC** (14.5%), PS (13.6%) PP (9.3%)	14.5%	Polymer spectral database	[62]
Surface and midwaters and sediments from Nakdong River, Korea	<20 µm	35% H_2O_2 and Fe (II) solution at 75 °C	lithium metatungstate (LMT)	ATR-µ-FTIR	Water samples: PP (41.8%), polyester (23.1%), PE (9.4%), PA (5.8%), PS (2.1%), alkyd (4.2%), acrylic (3.2%), poly(ethylene-vinyl) acetate (2.6%), PU (1.4%), **PVC** (1.1%), poly(acrylate styrene) (1%)	Water: 1.1%	–	[63]
					Sediment samples: PP (24.8%), PE (24.5%), polyester (5.5%), **PVC** (5.4%), PS (5.3%), acrylic (4.6%), polydimethylsiloxane (4.5%), PU (3.9%), polyacrylate-styrene (3.7%), poly (lauryl acrylate (3.6%)	Sediment: 5.4%		
Waters and sediments from Pearl River catchment, China	<0.1–5 mm	Water samples: 30% H_2O_2 Sediment samples: freeze-dried	Potassium formate (1.5 g/cm^3)	µ-FTIR (randomly selected particles confirmed with Raman spectroscopy)	PP (38.1%), LDPE (31.1%) (PP + LDPE + PE-PP + HDPE summed up to 64.5–83.7% of the total MP), PET, PS, **PVC,** PVA, PA, EVA, PMMA, ABS …	≈1%	Commercial polymer database	[64]
Surface waters and sediments of estuaries at Bohai Bay, China	0.15–5 mm	30% H_2O_2	NaI	Microscope + ATR-FTIR	Surface waters: PP (40%), PE (24%), PS (24%), **PVC** (4%), PET (4%), copolymerization mixture (4%)	Waters: 4% (1 particle)	Spectra of standard polymers	[65]
					Sediments: PE (39.5%), PP (21%), PS (29%), **PVC** (2.63%), PET (5.26), copolymerization mixture (2.63%)	Sediments 2.63% (1 particle)		
Seawater, fish and coral samples in a reef of Xisha Ilands, China	<6 µm to 5 mm	Fish: 10% KOH	NaCl	Microscope + ATR- µ-FTIR	Seawater: Rayon (64.8%), PET (7.3%) Fish: Rayon fibers (31.2%), PET fibers (16.5%), PA fibers (11.9%), PTFE (9.2%) Coral: rayon fibers (32.3%), PET fibers (15.5%), **PVC** fibers (14%)	14% (fibers in coral samples)	Commercial database	[66]
Sediments from Persian Gulf beaches	0.3–5 mm	0.05 M Fe(II) solution + 20 mL of 30% H_2O_2, at 75 °C	lithium metatungstate (1.6 g/mL) solution and a second separation with NaCl after treatment with Fe (II) and H_2O_2	Microscope + hot needle + ATR-FTIR	PS, PE, PET, PP	Not found	–	[67]

(*continued on next page*)

Table 1 (*continued*)

Sample matrix	Microplastics Size	Extraction/purification method	Density separation	Identification technique	Polymers found	PVC abundance	Library comparison	Reference
Sediments from Mangrove soils of the Ciénaga Grande de Santa Marta, Colombian Caribbean	1–5 mm		solution of sodium hexametaphosphate (2.5 g L^{-1})	Microscope + ATR-FTIR	PE, Acrylonitrilie butadiene rubber (NBR) and methaqualone	Not found	Commercial reference libraries	[68]
Sediments from Slovenian beaches	100–2000 μm	preserved in 70% ethanol until polymer analysis	NaCl	ATR-FTIR	PET, PE, PP, styrene acrylonitrile resin, PS, expanded PS, nylon 6 and epoxy polyester resin	Not found	customised polymer library	[18]
Sediments from Datça Peninsula, Turkey	1–5 mm	H_2O_2 30%	NaCl	Microscope + ATR-FTIR	SBS (60%), PS (33.3%). The same samples being pressed and slenderized: PE (58.4%), PP atactiv (12.5%), nylon II (12.5%9, ethylene Propylene Dien Monomer (EPDM 12.5%), polyvinylidene chloride (PVCD 4.1%)	Not found	–	[69]
Deep sea sediments from the Artic Central Basin	>100 μm	Dried at 60 °C 96 h	105 mL of sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, 40% w/v, density 1.4 g cm^{-3})	Microscope + μ-FTIR (>100 μm)	Polyester (n = 3), PS (n = 2), polyacrylonitrile (n = 1), PP (n = 1), **PVC** (n = 1), PA (n = 1)	1 particle (11%)	Standard polymers	[70]
Water and sediments in a coastal metropolis in Australia	>20 μm, 1.2 mm average	NaOH (2 M) at 55 °C for 48 h.	NaCl (sediments)	Microscope + μ-FTIR	Polyester, PP, PA, PE, **PVC**, PS, acrylic, rayon, PP-PE, PC …	≈5% sediments, ≈1% water	Commercial database	[71]
Biota (shrimps) of Bengal, Bangladesh	<250 μm - 5 mm	30% H_2O_2	NaCl	Microscope + μ-FTIR (30% of total MPs)	PA-6, rayon	Not found	Reference spectral library	[72]
Sediments of urban and highway stormwater retention ponds in Denmark	10–2000 μm	15% H_2O_2 at 50 °C and Fenton reaction by adding 146 mL 50% H_2O_2, 63 mL of 0.1 M $FeSO_4$, and 65 mL of 0.1 M NaOH after the density separation	$ZnCl_2$	μFTIR imaging (<500 μm and Microscope + ATR-FTIR (>500 μm)	PP, PS; polyester, PE, PU, **PVC**, acrylic, PA and other in low percentages	>5%	MPhunter reference spectra and reference polymer libraries, including that developed by JPI-OCEANS-BASEMAN project	[21]
Mussels (*Mytilus galloprovincialis*) from Turkish coast (Black Sea, Sea Marmara and the Aegean Sea)	70 μm–5 cm	Digestion with H_2O_2 (30%), 3 days at 65 °C	–	Microscope and confirmation with FTIR	12 types of polymers identified, including PET 33%, EVA, PA, polyacrylic (PAC), PC, PE, polyacrylonitrile (PAN), PS, PP, **PVC**, polyvinyl fluoride (PVF), cellulose acetate (CA)	2.25%	Reference spectral library	[73]
River water from Yulin River, China	64–5000 μm	Digestion using 30% H_2O_2 (first, digestion at 60 °C for 1 h; second, digestion at 100 °C for 7 h)	–	Microscope + Nile Red solution. Some particles characterized using μRaman	PE (39%), PP (31%) and PS (23%)	–	–	[74]
Water and sediments from the Elba river, Europe	Water: 150–5000 μm	Water: digested with 1:1 mixture of 10 M KOH solution and H_2O_2 (30%).	Water: Density separation with potassium formate (density: 1.6 g mL^{-1}).	Visual identification, verification with pyr-GC–MS (particles 20–125 μm, sediments) and ATR-FTIR (particles >500 μm and selected smaller ones)	Water: PE (47.5%) and PP (45.0%).	–	Built-in polymer databank and reference spectra of most common polymers	[75]
	Sediments: 20–5000 μm	Sediments: fraction of 125–1000 μm density separation and then digested with 10:1 mixture of 30% H_2O_2 and 10% H_2SO_4, 5 days, 55 °C.	Sediments: density separation in a custom system filled with $ZnCl_2$ ($\rho = 1.6–1.8$ g cm^{-3})		Sediments: PE (34.4%) and PP (12.5%), PS (18.5%) and ABS, PA, PET and PMMA (in total 2.0%)			

Freshwater and wild fishes from Lijiang River in Guangxi, S.W. China	>75 µm	Water: digested with H_2O_2 (30%) at 50 °C, and then density separation with saturated NaCl. Fish: digestion of gastrointestinal tracts and gills with H_2O_2 (30%) at 65 °C.	NaCl (water)	Microscope and suspected particles verified by µFTIR	Water: copolymer PP/PE (37.6%), PE (32.2%), PP (19.1%), PB, **PVC**, PS, PET, PA and polyether sulfone (PES). Fish: PET (most abundant), PP, PS, PP/PE, **PVC**, PE.	<1%	Built-in library of polymers	[76]
Surface water of Lake Victoria (East Africa)	0.3–4.9 mm	Digestion with H_2O_2 (30%) in the presence of 20 mL of 0.05 M acidified ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) catalyst.	NaCl	Microscope and the “break test” and “hot needle test”. FTIR for 20% of particles	LDPE, HDPE, PP, PS and PES (polyester)	Not found	Polymer library	[77]
Beach sediments from S.E. coast of South Africa	Fibers: 292 –5830 µm Fragments: 111 –1846 µm Films: 184 –2222 µm	Digestion with H_2O_2 (30%)	$ZnCl_2$	SEM and ATR-FTIR	PP, PC, PES, Rayon (RY), nylon (NY), Polyacrylonitrile (PAN), PS, LDPE, HDPE	Not found	Polymer library	[78]

isolated MPs from water, sediments and biota by means of widely different procedures and identified/quantified them with different analytical techniques, mainly IR and Raman spectrometry. In the following, the most relevant steps of the commonest analytical methodologies are reviewed to seek for the main phenomena that may lead to an underestimation of the amount of PVC. A current challenge when searching for MPs is the lack of standardized protocols for sampling, extraction, identification and characterization of MPs. The use of digestion steps (or not), different mesh sizes or the various spectroscopic measurements may all constitute sources of relevant variability between studies [7].

With regard to sampling, the density of the MPs determines their distribution in the water column. In general PVC is denser than water so it tends to sink (although that can be affected by weathering, biofouling, aggregation, etc.) [21]. Thus, PVC is expected to be found in sediments more than in water [7]. Nevertheless, as Table 1 shows, PVC was only found in 11 out of 26 sediment marine studies, and even then PVC was detected in very low percentages (much lower than its production figures).

4.2. Digestion-based separation

Regarding sample pre-processing, many possibilities were reported for MPs extraction and purification, including reagents and equipments/devices. Among the latter, ultrasonication, microwaves, filtration systems, and sieving outstand [11]. Digestion protocols are required when environmental samples are rich in biologic material or when determining the exposure of organisms. Thus, organic matter removal procedures have been developed considering (depending on the matrix) acid, alkali, oxidative, enzymatic and mechanical treatments (or their combination). The most frequent reagents were HNO_3, HCl, NaOH, KOH, H_2O_2, $ZnCl_2$, $CaCl_2$, and enzymes (also with many options, like trypsin, protease, collagenase and pepsin, and their combinations), However, not all of them remove organic matter without damaging the polymers (their surface porosity, colour fading, etc.) [11,14,22].

As Table 1 shows, HNO_3, KOH or H_2O_2 (the latter alone or combined with Fe (II) –Fenton reaction), are frequently used, even combined with relatively high temperatures (≥70 °C). Nevertheless, they have drawbacks as several studies demonstrated diverse alterations of polymers after the use of acids [14]. For instance: the destruction of some polymers with low pH tolerance when using H_2SO_4 and HNO_3. Nam Ngoc et al. [7], reported 3.3% recoveries of spiked MPs of PVC in sediments after using HNO_3 to oxidize organic matter; probably because its reaction with the surface of the MPs changed their surface properties.

H_2O_2 is a common workhorse and 36 out of 53 studies reviewed in Table 1 reported its use, either alone or combined with other reagents. However, it is a powerful bleaching agent that can alter plastic particle color and impede visual identification [5]. Previous works reported that H_2O_2 at 50 °C decreased the recovery rate of several polymers [23]. The use of 30% H_2O_2 can lead to uncontrolled exothermic reactions and foam production, which may potentially cause loss of MPs [21]. Despite high temperatures may help reducing the time needed for a full digestion of biological material they can damage polymers [19]. Wiggin et al. [24] noted that high temperatures (60 °C), high H_2O_2 concentration (30%) and large incubation times (24 h) yielded colour loss in the synthetic materials and warping in the filtering units.

Alkaline treatments, like those using potassium hydroxide at 50 and 60 °C reduced the recovery rate of PVC [23].

In general, it seems that the enzymatic procedures, along with KOH and H_2O_2 (the latter two when used at low concentrations and low temperatures) are effective and “plastic friendly” methods to remove the organic matter from marine environmental samples.

4.3. Density separation

Regarding the separation/extraction of the MPs from the sedimentary matrices, it is done usually by means of density separation [14]. Most studies used oversaturated solutions of NaCl, NaI, $CaCl_2$ or $ZnCl_2$, with or without centrifugation. The commonest one being NaCl thanks to its low prize, ready availability, eco-friendly behaviour and because it yields reproducible MPs isolation. Indeed, 53% of the works compiled in Table 1 that used saturated solutions employed NaCl. It allows for the separation of materials with densities up to 1.2 g cm^{-3}, which includes the most common polymers but not PVC (1.38 g cm^{-3}). Table 2 compares the densities of polymers encountered commonly in the marine environment and common oversaturated solutions. Zinc chloride, sodium bromide, zinc bromide, sodium iodide, or sodium/lithium polytungstate reach higher densities than sodium chloride [25,26]. Nevertheless, the former two are highly toxic for the environment, and the latter three are very expensive [26]. NaI can be a good alternative considering its density (1.80 g cm^{-3}) and moderate toxicity and price. Other works that analysed sediments and seawater samples, applied denser solutions, like $ZnCl_2$. However, they still found very low percentages of PVC although, surprisingly, denser polymers like PET -1.4 g cm^{-3}- were reported frequently (Table 1), even when using NaCl. This fact can be only attributed to the use of polymer libraries without weathered spectra of PVC.

4.4. Identification technique

With respect to the analytical identification technique, a correct selection is of utmost importance. In many studies MPs were “identified” using optical microscopic observation only, without further chemical characterization. Although it is true that optical microscopy is still a powerful, and frequently used, tool for particle visualization it is not a good way to ascertain the nature of the particles (polymers) nor to quantify them. In fact, most studies reviewed in Table 1 used microscopy to isolate the MPs before their spectral identification. However, as MPs can be easily confused with organic debris, inorganic particles, and other particles, the risk of under/overestimation with optical microscopic observation is significant. Visual underestimation of PP and PVC was attributed to the loss of small particles [27,28]. The same remarks can be given to the so-called hot needle test, which was demonstrated to be not as good to assess MPs [11].

Hence, the application of spectroscopic instruments to perform a chemical identification of potential MPs is a must. For example μFTIR imaging combined with automated MP identification minimizes false negatives and reduces human bias in the analytical procedure [21]. When compared to manual analysis, a seven-fold increase in the number of polymer particles can be found with the automated analysis. This no doubt is of relevance when the underestimation of PVC MPs is to be explained.

The most frequently used techniques for MPs characterisation are FTIR (or simply, IR) and Raman spectroscopy as they enable the chemical identification of the polymers and their differentiation from debris. Importantly, differences in polymer crystallinity, chemical functional groups and weathering can be detected efficiently [11]. FTIR and/or μFTIR were applied in 85% ($n = 43$) of the works reviewed in Table 1, although scarcely 47% of them found PVC (whether in very low percentages). It is worth noting that despite only 19% of the revised studies used Raman or μ-Raman ($n = 10$), up to 70% of them found PVC.

Undoubtedly, the usual practice of measuring a part of the filter or a sample aliquot will magnify largely the errors when reporting MPs abundance [7]. The application of automated (or semi-automatic) techniques (as μFTIR or μ-Raman imaging) will reduce the analysis time and improve MPs characterization, although they are very expensive and not without practical difficulties.

Some authors reported that after ATR-FTIR analysis, only 11.3% of the putative MPs were clearly confirmed as such, 4.3% of the particles were organic material and 76.2% became unidentified; 8.2% showed plastic characteristics but failed ATR-FTIR validation. This fact was attributed to the changes induced by weathering on the particles, which may hamper the IR identification of the polymer [18]. In this way, Hidalgo-Ruz et al. [29] reported that false positive results could represent up to 70% of all assumed microplastics. In previous studies, these falsely positive particles ranged from less than 10% to about 98% of the separated particles [18]. Sample deterioration/degradation explains that particles that visually showed clear properties of synthetic material, could not be verified as such by ATR-FTIR spectroscopy [18]. Again, the need for using spectral libraries containing aged plastics is evident. This is reinforced by reports such as that from Hendrickson et al. [30] who compared the identifications of 19 particles analysed both with pyrolysis-gas chromatography-mass spectrometry (Pyr-GC-MS) and with ATR-FTIR. For the latter, the most frequent polymer was PE, while for the former PVC was the most common one. This inconsistency was attributed to the heterogeneous chlorine content occurring during the chlorination of PE and PVC, and to the broad number of possibilities of plastic polymers, copolymers, and additives, in addition to natural processes that can alter the particles, including photo-oxidation and degradation.

Similar to FTIR, a main limitation of Raman characterization is sample degradation, as stated when studying PVC [27]. In effect, the PVC spectra after photo-degradation showed a simultaneous

Table 2
Densities of common polymers and common density separation solutions (adapted from Frias and cols [26]).

Abbreviation	Polymer	Density (g cm^{-1})	Adequate saturated solution
PS	polystyrene	0.01–1.06	NaCl (1.0–1.2 g cm^{-3})
PP	polypropylene	0.85-0.92	
LDPE	Low-density polyethylene	0.89-0.93	
HDPE	High-density polyethylene	0.94-0.98	
PA 6,6	polyamide	1.13-1.15	
PMMA	Polymethyl methacrylate	1.16-1.20	
PC	polycarbonate	1.20-1.22	$Na_2WO_4.2H_2O$ (Sodium tungstate dehydrate,1.40 g cm^{-3}); NaBr (1.37–1.40 g cm^{-3}); $3Na_2WO_4.9WO_3.H_2O$ (sodium polytungstate, 1.40 g cm^{-3});
PU	polyurethane	1.20-1.26	
PET	Polyethylene terephthalate	1.38-1.41	$Li_6(H_2W_{12}O_{40})$ (Lithium metatungstate, 1.6 g cm^{-3}); $ZnCl_2$ (1.6–1.8 g cm^{-3}); $ZnBr_2$ (1.71 g cm^{-3}); NaI (1.80 g cm^{-3})
PVC	**Polyvinyl chloride**	**1.38–1.41**	

intensity reduction of the peaks at 693 and 637 cm^{-1}, which corresponds to the characteristic C—Cl bonds of the polymer. Therefore, the idea of including spectra of weathered polymers (even at different ageing stages) in reference spectral databases to obtain reliable identifications of the polymers that may constitute the MPs is strongly reinforced.

5. Conclusions

The chemical characteristics of PVC may cause that its presence in the environment becomes underestimated. The changes that environmental weathering causes at the surface of PVC microplastics, or to the additives added to this polymer (whose quantities amount up to percentages), change its spectral profile, which difficult its straightforward identification by infrared spectrometry. Thus, the knowledge about how PVC evolves in the environment and how this reflects in the spectra is very important.

Furthermore, the fact that different types of (complex) sample treatments are required before the suspicious microparticles can be characterized chemically implies that they are also sources of eventual surface degradation. Some general, practical recommendations can be given here. With respect to the flotation options, the common usage of saturated NaCl seems not the best option to cope with PVC and NaI seems a good alternative, economically and environmentally friendly. With regards to sample digestion, the use of aggressive reagents or harsh analytical conditions must be avoided. Enzymatic alternatives are a good option, although expensive and slow. The alkaline + oxidative alternative offered by KOH and H_2O_2 is recommended although temperatures should not exceed ca. 40 °C and concentrations should be within the 15—30% range. Caution should be taken when using the Fenton's reagent as temperature raises and much foam is formed. Considering the identification step, PVC and PE can be differentiated at the 1500-900 cm^{-1} fingerprint region, which has much less peaks/bands for PE. If the particle under study is big enough (>500 μm), consider scrapping its surface or cutting it to measure its centre, as it will not be affected by weathering. Remember that it is of paramount importance to use customized spectral databases including spectra of aged PVC, preferably at different weathering extents. Finally, for quantifying microplastics, if possible, do not extrapolate the number of particles from a small area to the whole filter, in order to avoid magnifying possible misidentification errors. Thus, it is expected that these measures will contribute to harmonise the analytical procedures and to increase confidence when reporting PVC (or its absence) in environmental monitoring and assessment of the ecological impact of microplastics in the marine environment.

Declaration of competing interest

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

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