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Microplastic aging processes: Environmental relevance and analytical implications

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ABSTRACT

The analysis of microplastics (MPs) in terrestrial environments and the evaluation of their environmental risk has gained great attention, owing to the increasing evidence for their widespread presence in soils and freshwater sediments globally. Once in the environment, MPs undergo abiotic and biotic processes which alter their properties and integrity: this process is called "aging" and has implications for the fate of these contaminants, their morphology and surface chemistry. Aging may also affect the analytical assessment of MPs in environmental samples which likely contain aged MPs. In contrast, analytical methods are established using pristine plastics for validation. This can lead to uncertainties in quantification and characterization. This critical review summarizes the current trends in the simulation and characterization of MP aging in laboratory conditions, highlighting limitations and knowledge gaps. It also discusses the challenges in MP analysis induced by aging in environmental samples, providing directions toward possible solutions.

1. Introduction

Plastic pollution is an environmental threat of global relevance. Plastic, and especially microplastics (MPs, fragments with dimension between 1 and 1000 μm [1]), are widespread in the environment. Nine to 23 million metric tons of plastic are estimated to reach the oceans every year [2]. However, this represents less than 3 % of total mismanaged plastic waste [3]. In contrast, the load of mismanaged plastic released to land and freshwaters is tenfold higher (30 % of the total [4]). This load accumulates primarily in freshwater sediments and soils. The broader environmental impacts of this contamination, however, remain unclear [5–8].

Once plastic is dispersed in these compartments it undergoes a series of processes collectively resulting in aging (this process is also referred as weathering or degradation). These processes may be divided into two main categories: abiotic and biotic processes. The former includes reactions with physical-chemical agents affecting polymer matrix integrity and chemistry (e.g., light irradiation, physical abrasion, thermo-chemical oxidation), while the latter includes the processes leading to the formation of a "corona" (or biofilm) of microorganisms [9,10]. While biotic and abiotic aging processes act simultaneously, the prevalence of a given process can vary upon the environment in which plastic is dispersed (e.g., in different environmental matrices) and the chemical composition of the plastic [5,10]. All these processes alter the surface properties, reactivity, propensity to embrittlement, and more generally the environmental fate (and possibly toxicity) of plastic fragments [5,11,12].

Environmental effects of MP aging have already been summarized in several recent reviews (e.g., Refs. [7,10,13–18]), but some key knowledge gaps still need to be filled. In this review, we will summarize the current knowledge and the future steps toward an environmentally relevant simulation of aging processes and how these will help in understanding the environmental implications of MP pollution. Here we will also highlight a missing link in the study of environmental aging of MPs: the potential influences of this process on the accurate analysis of MP concentrations or characteristics in environmental samples. In fact, beyond the environmental consequences induced by plastic aging (e.g., changes in behavior and surface properties of MPs), the alterations induced by aging processes carry a series of implications for the analytical methods used to purify, concentrate, and analyze MPs in environmental samples. Setting up analytical protocols and harmonizing

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Abbreviations

AFM	atomic force microscopy
BET	Brunauer Emmett Teller
CLSM	confocal laser scanning microscopy
DNA	deoxyribonucleic acid
DSC	differential scanning calorimetry
EDX	energy dispersive X-ray spectroscopy
EGA	evolved gas analysis
EPS	extracellular polymeric substances
FTIR	Fourier transformed infrared spectroscopy
GC	gas chromatography
H_2O_2	hydrogen peroxide
HNO_3	nitric acid
ICP-MS	inductively coupled plasma - mass spectrometry
KOH	potassium hydroxide
LA	laser ablation
LIBS	laser-induced breakdown spectroscopy
MALDI-ToF-MS	matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
MP	microplastic
MS	mass spectrometry
NaOH	sodium hydroxide
PE	polyethylene
PET	polyethylene terephthalate
PLA	polylactic acid
PP	polypropylene
PVC	polyvinyl chloride
PS	polystyrene
Py-GC-MS	pyrolysis - gas chromatography - mass spectrometry
SEM	scanning electron microscopy
STXM	scanning transmission X-ray microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
ToF-SIMS	time-of-flight secondary ion mass spectrometry
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

MP analyses of environmental samples – especially for carbon rich sediments and soils – have represented a challenging endeavor. Methods need to provide high reliability, sensitivity, and effectiveness while facing the daunting heterogeneity in polymer types, chemical additives, shapes, and sizes characterizing the particles present in environmental samples [19,20].

Analytical protocols are generally established and validated using virgin, unweathered MPs, which present different physical and chemical features compared to aged environmental particles [21]. This adds further challenges and implications for analysis and increases the uncertainties in the characterization of MPs in environmental samples which, to date, have not been sufficiently addressed. A marginal number of studies recently tried to observe the effects of MP aging on the recoveries and analytical capacity of newly developed methods (e.g., Refs. [22,23]), especially in comparison to the extensive research effort put into analyzing MP in several environmental media (e.g., Refs. [19,24]).

In this critical review, we will first summarize the environmental processes related to aging and the best strategies to create simulated aged materials. We will then review the environmental implications of MP aging, with a focus on the knowledge gaps and the available analytical tools to characterize the effects of aging processes on MP properties. Finally, we will examine the main implications for the analytical assessment of MPs in real environmental samples associated with their aging. We will conclude by proposing ways forward to overcome some of these issues.

2. Aging processes and their experimental simulation

The simulation of environmental processes and agents affecting MP weathering is a key step toward the understanding of MP environmental aging and the creation of environmentally realistic standard reference materials. Aged MP reference materials may be used for the validation of new analytical methods, quality assurance and control, as well as in fate and effect studies.

Aging processes are generally simulated in simplified laboratory conditions or through long-term semi- or un-controlled field exposures. These processes vary upon the environmental conditions in which MPs are generated or dispersed: the diverse aging agents can in fact act differently depending on the local climate and other environmental factors (e.g., light exposure is different along depth in the water column or in soil environments). Experiments are therefore designed to cover specific environments and aging processes [25]. Here we will review aging studies for terrestrial natural environments (i.e., freshwaters and soils).

2.1. Laboratory-based aging studies

Laboratory based methods to simulate MP aging are variable: several different environmental processes are simulated in literature (Table 1). The most frequently used approach is ultraviolet (UV) irradiation, which simulates the photoinduced oxidation of plastic polymers due to sunlight exposure [15,16]. This process is simulated under a wide range of conditions: at various radiation intensities, durations, and temperatures [26]. Polymer oxidation can also be simulated with other physical and chemical stressors, such as ozone [25], chemical oxidants in solution (e.g., hydrogen peroxide-H_2O_2, Fenton's reagent, and sodium hypochlorite [27,28]), and thermally induced oxidation [29]. UV oxidation experiments are still the most frequently utilized approach, likely because of the simplicity of their experimental setup [26,28]. However, some drawbacks arise in the use of UV oxidation processes to generate aged MPs, such as: i) the variable exposure conditions tested complicates the comparison of findings among different studies [26]; ii) oxidation induced by UV radiation heterogeneously affects the bulk material even at constant light radiation; and iii) plastic objects are loaded with UV filters or other types of antioxidants to reduce the direct oxidation of the polymers [30], while MPs tested are usually additive-free industrial pellets or spheres [21,26].

Besides oxidation, other aging processes inducing chemical changes in plastic (e.g., hydrolysis) have also been studied. Hydrolysis processes are observed to favor the scissions of ester bonds in the environment [10]: this process is simulated in laboratory by catalyzing the acidic or alkaline hydrolysis [15]. Variable chemical and physical conditions are also tuned in more sophisticated experimental settings, where other chemicals are used in combination with the main oxidative chemical or photochemical agent [10,31]. These approaches are conceived to improve the environmental relevance of the aging processes and of the obtained aged plastics. However, more complex aging conditions may blur the possibility of tracking the effects of different agents, resulting in a loss of information and control.

Mechanical stress is another abiotic agent simulated in laboratory experiments. Aging is performed by adding a frictional force, typically through shaking or sonication in batches containing other solids (e.g., sand [32,33]). This type of aging simulates important environmental factors affecting terrestrial MPs. However, these types of laboratory assessment are still relatively rare.

Finally, lab-based works have also addressed biotic aging of MPs

Table 1
Summary of the most used experimental aging processes, showing the simulated environmental agents and studies applying the indicated approaches with a brief description of the experimental setup proposed.

Aging process	Simulated environmental agents	Experimental setups	Reference
UV aging	Sunlight exposure	Exposure to UV lamps with different wavelengths in air and water for 16 days	[35]
		Exposure to UV-C lamps in air for 25 days	[36]
		Exposure to UV-C lamps for 4 days in air and ultrapure water and exposure with a solar radiation simulator for 5 days	[25]
		Exposure of MPs to UV-A lamps for 10 days in air	[37]
Chemical oxidation	Chemical stressors in water bodies Sunlight exposure	Ozonation treatment in air and bubbling in ultrapure water	[25]
		Incubation of MPs with H_2O_2 and Fenton reagent for 7 days	[38]
		Treatment with potassium persulfate and treatment with Fenton reagent for 30 days	[39]
Thermal oxidation	Temperature changes Sunlight exposure	Addition of plastic in a climate-controlled chambers and exposure at 30, 40 and 50 °C	[29]
		Addition of plastic in a heat oven at 90 °C for 30 days	[40]
Other chemical treatments	Hydrolysis in freshwaters Strongly acidic or alkaline conditions (e.g., wastewater treatment plants) Effect of other chemicals in water	Immersion of plastic in different reagents (i.e., sodium hydroxide – NaOH 0.1 M, nitric acid – HNO_3 0.1 M and H_2O_2 33 %) and in environmental freshwater coupled with exposure to UV-A radiation for 10 days	[31]
		Aging in HNO_3 0.1 M In dark and in combination with UV-C for 15 days	[41]
Mechanical stress	Stress due to longitudinal transport and contact with other solids (e.g., sand)	Mechanical stress of MPs in water solution with ultrasonication for 1 h	[32]
		Deployment of MPs in amber glass bottles with quartz sand (grain size <500 μm) in an orbital shaker for 90 days	[33]
Biotic aging	Colonization by microorganisms on plastic surface	Incubation of MPs with a *Chlorella vulgaris* algal strain and with a freshwater environmental sample for 30 days	[42]
		Incubation of MPs with 25 different seawater unialgal cultures for 6 weeks	[43]
		Incubation with a synthetic community including 3 freshwater algal species for 10 days	[44]

through studies of the formation of a microorganism corona on MP particle surfaces. These experiments are typically performed through the incubation of MPs with artificially assembled consortia of microorganisms or inocula obtained from the environment [31,34]. However, creating realistic biofouled MPs in a reproducible manner is challenging, especially when working with assemblages of multiple species. This requires tight control over several variables (e.g., nutrient concentration and pH in the growth medium, consistency of inocula, mixing rate of the solution, light). To reduce complexity, some studies have focused on growing mono-species biofilms [31]. This can help to achieve more reliable and predictable aging across different batches, but with a trade-off on the limited environmental representativeness of the obtained MPs.

2.2. Field-based aging studies

Aging studies conducted under the field conditions can consistently replicate the natural processes that occur to plastic dispersed in the environment, such as the ones listed in Table 1. A clear benefit of implementing field-based studies over laboratory simulations is their ability to replicate or utilize actual environmental processes. The high environmental realism is gained with the loss of environmental control: results are in fact strongly location dependent. It has been suggested that studies should be replicated in multiple locations and in different periods of the year to obtain more generalized results [26].

Field studies for MP aging are very frequent in aquatic environments. Here, the uncontrollable field conditions generate potential complications. For example, the occurrence of moving waters or currents can lead to the potential loss of materials [45]. As a result, controlled systems are needed to maintain the experimental setups (such as the use of submerged enclosures and cages), with a potential reduction in environmental relevance, for example by limiting light exposure of floating MPs which were forcibly submerged [46].

Studies focusing on the aging of MPs in soil ecosystems under field conditions are still lacking instead [6,18]. This paucity of information represents an important knowledge gap, particularly given that some preliminary studies have indicated that the majority of MPs may be retained by some soil types (e.g., Ref. [47]). Difficulties in replicating several environmentally relevant processes in the laboratory has also already been reported, for example, with respect to differences in plastic biodegradation rates in laboratory vs field experiments (e.g., Ref. [48]).

3. MPs changes in properties after aging: current knowledge gaps and research needs

The changes induced by aging processes have implications for the potential toxicity and behavior of MPs, as well as for their analytical assessment. In this section, we summarize the main trends related to alterations of MP properties by different abiotic and biotic aging agents, alone or in combination, including a consideration of the implications which may be expected for their study in environmental (analytical) chemistry. Within the context of this review article, we will mainly focus on the knowledge gaps related to MP aging effects.

3.1. Surface chemistry

Changes in surface properties are important in defining the tendency of MPs to form aggregates, as well as to transport various chemical species in the environment [49]. This can in turn affect their potential toxicity [5,7,50]: gaining control on MP aging mechanisms is therefore fundamental to achieve effective ecological risk assessments of plastic pollution in terrestrial environments.

The chemical mechanisms of photo- and thermo-oxidation and the consequential effects on surface properties (especially for several conventional polymers such as polyethylene – PE, polypropylene – PP, polystyrene – PS, polyethylene terephthalate – PET) are well known [13,

28]. The surface of aged alkyl polymers (i.e., PE and PP) is characterized by an enrichment in oxygen-containing functional groups (especially carbonyl and hydroxyl groups), increased hydrophilicity, and a shift toward a more negative surface charge in comparison with pristine polymers [7,16,35]. Less marked changes of this kind in polyesters (such as PET) are ascribable to different degradation mechanisms (i.e., Norrish type I and II, hydrolysis) and also to the fact that these polymers have oxygen-containing functional groups already in their pristine form [10]. These changes increase polymer wettability and the negative surface charge of MPs (Fig. 1 a, [5,7]), and are reported to make MPs more prone to sorb hydrophobic compounds and metals in aquatic solutions [51,52].

Data concerning changes in surface properties from chemical or photo-oxidative processes in biodegradable polymers are instead scanter and more fragmentary. As an example, UV aging of polylactic acid (PLA) has shown unclear trends: while some reports show that UV aging results

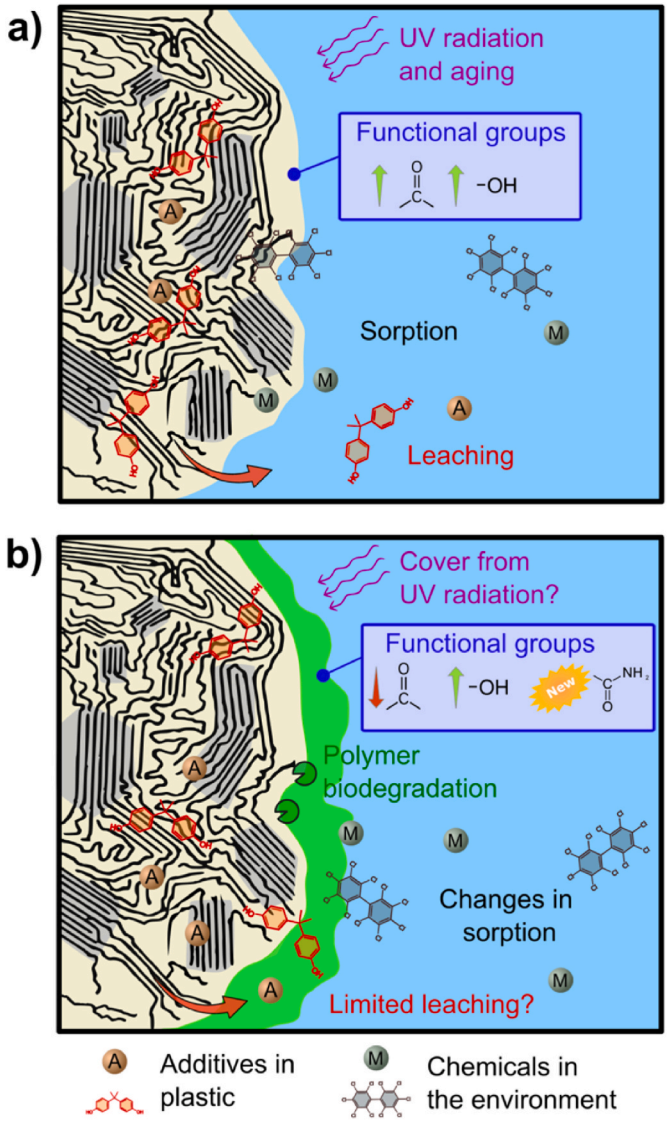

Fig. 1. Conceptual model of the "cover effect" of biofilm, including the relevant environmental implications, exemplified in an aquatic setting (Modified from Ref. [5], content under creative common license). In panel a, an example of environmentally aged MP without a developed biofilm is shown, with MPs exposed to light radiation and enriched in oxygen containing functional groups. In the case of biofilm covered MP (panel b), instead, the surface functional groups of the biofilm dominate the chemical interactions, and the biofilm may "cover" the effect of light, as well as mediate sorption and leaching processes.

in oxidation processes comparable with other polymers (such as PE and PP), other studies find limited (or absent) changes of aged polymers in comparison to pristine polymers of the same type [36,44]. A possible explanation is that other processes (e.g., hydrolysis) prevail, acting at a faster rate in degrading the polymer compared to photooxidation. Also, the potential different load of anti-oxidants and UV filters added to these biodegradable materials can likely play a role [53]: the different load of additives in samples of the same polymer analyzed in different studies may justify the different experimental outputs.

The development of a biofilm or so-called "eco-corona" on the surface of MPs also yields significant changes in the surface properties. The biofilm comprising microorganisms such as algae and bacteria and their extracellular polymeric substances (EPS) completely changes the surface properties of MPs, acting as a "cover effect" and masking the surface features of the pristine polymer (Fig. 1b). The surface is generally enriched in peptides, hydroxyls, and polysaccharides by corona formation, while some studies reported a reduction in carbonyl groups after biotic aging [7,31,44]. These changes also provide additional binding sites for complexation and decrease surface hydrophobicity [54,55]. This significantly changes the sorption properties for other pollutants. Ionic compounds and metals may be more strongly sorbed by the biofilm matrix [5,11,44]. Hydrophobic contaminants may also passively diffuse in microbiological tissues, but the biological matrix may affect uptake rates posing an additional resistance at the interface between the plastic and soil particles or water films [42,56,57]. For example, natural organic matter coatings on PS and PE MPs has been shown to reduce sorption of antibiotics by blocking potential sorption sites at the surface of the plastic [51,58]. The organism composing the biofilm community may also metabolize and possibly degrade the absorbed chemicals.

The biofilm on the surface of MPs can also be associated with initial surface physical degradation causing cracks and singularities, potentially increasing the surface are of MPs [7,46,59]. Biofilm exudates may in fact favor hydrolysis, and bacteria may use plastic as a carbon source [60]. On the other hand, the presence of biofilms can scatter the UV light which would otherwise further degrade the polymer matrix. In fact, UV radiation penetrates poorly into the matrix of biofilms, and only the first few top layers of microbial cells are exposed, leading to a minimal irradiation of the plastic polymer [46,61,62].

3.2. *Effect of aging on mechanical properties and fragmentation*

Aging processes promote the loss of mechanical properties of MPs: chain scissions and heterogeneities induced by aging cause the embrittlement of polymers [37]. The polymer type and chemical additive composition is a determinant of the propensity for embrittlement under environmental stress. For example, PP is observed to be more prone to embrittlement after the physicochemical oxidation of the polymer matrix compared to PE, PET, PS, and polyvinyl chloride (PVC) [63]. Similarly, biodegradable polymers are more prone to mechanical properties loss in comparison to polyolefins [64]. However, a direct comparison of different polymers is difficult to perform in a meaningful way due to different experimental processes, as well as different formulations of plastic tested for aging (e.g., variable loadings of additives and polymer post-processes for plastic objects production).

The role of abiotic aging on the fragmentation rates of plastics instead presents substantial knowledge gaps. The formation of MP from aged meso- and macroscopic items is a key process controlling sources and concentrations of MP in the environment (e.g., Refs. [32,65–67]). However, the degradation pattern of generated MPs in the environment is still unclear. Hypothetically, fragmentation of MP into smaller debris results in higher reactive surface area and possibly further promotes fragmentation [68]. On the other hand, fragmentation rates may decrease after reaching a small critical size: smaller fragments are expected to require stronger mechanic energy or specific mechanic stress routes (e.g., by interaction with solids with adequate small roughness scale) to be further fragmented [69,70]. Also, biotic aging may be

limited under a critical small size threshold, in which living microorganisms can no longer be stably hosted on the fragment surface [71]. In summary, while progressively smaller sizes can enhance the effectiveness of photochemical degradation processes, they may hinder mechanical and biological degradation processes [72].

Biofilm formation has a significant effect on the mechanical properties of MPs too [11]. For example, MPs can form aggregates with other natural or anthropic particulates through biofilm formation [54,73]. This increases their size but also changes the overall particle density, as the density of natural biofilms and particles ranges from 1.1 to 1.5 g/cm^3 [74,75], while plastic polymer densities are generally lower (e.g., PE and PP range between 0.9 and 0.95 g/cm^3) or in fewer cases higher (e.g., PVC ranges between 1.1 and 1.6 g/cm^3). Such changes are particularly important for MP fate and transport processes [75], but also for their analysis in environmental samples.

3.3. Aging and chemical additives leaching

Changes in the polymer matrix induced by abiotic aging can affect the leaching of additives and monomers, as well as other compounds derived by polymer degradation. This in turn can have implications for particle toxicological properties. This process is favored after polymer aging owing to polymer oxidation and fragmentation, increasing surface area and wettability. These aspects have already been the subject of several studies [12,76].

The plastic polymer contains various chemical types with different molecular dimensions and chemical properties and, consequently, variable leaching rates. For instance, metals are often present as salts, oxides, and metal-organics, which are more likely to be released in the aquatic phase compared to hydrophobic chemicals, owing to their smaller molecular dimensions and possibly weaker interactions especially with aliphatic polymer matrixes [77–79].

Several organic compounds are reported to leach from aged MPs too. Collins et al. [80], for example, reported the increase of organic matter leached from five different polymers after 24 h of UV aging in comparison to pristine one. An important knowledge gap in this sense is that different organic chemicals present in the polymer matrix may be oxidized by UV radiation too [12]: the perfect example for this class of compounds are UV filters or anti-oxidants, which are designed to absorb UV radiation and reduce the aging process of plastic polymers (or prevent oxidation of the polymer chain) by reacting themselves with oxygen radicals or radicals produced by the initiation of the polymer chain fracture. Oxidation makes these compounds more hydrophilic (e.g., Ref. [81]) and therefore also possibly more prone to leaching. Other additives (e.g., flame retardants) can also be oxidized and become more susceptible to leaching in water [17]. This evidence highlights the importance of understanding aging mechanisms and considering the chemical composition of aged particles when studying MP toxicity.

Despite the extensive literature dealing with leaching of additives during abiotic aging, knowledge on the effects of biotic aging on leaching is much more limited [12]. The role of the eco-corona covering MPs is unclear: on one side it may mediate the release of chemicals from plastic, inducing, on the other side, a faster biodegradation of the polymer. As an example, Sheridan et al. reported the ability of plastic leachate to alter the bacterial community in experiments conducted with lake water [82]: this process may lead to the assemblage of a plastic-specific biofilm community selecting polymers as a carbon source [59]. On the other hand, toxic additives released by aged plastics can also reduce the colonization by sensitive microorganisms: abiotically aged MPs are in fact colonized to a limited degree by microorganisms in comparison to pristine ones. This effect, ascribed to the leaching of toxic chemicals after aging, was reported for algae after UV aging of three different polymers (PE, PP and PLA) and for tire wear particles [44,83].

It is also not clear how the dynamics of leaching may change after the colonization of MP particles by biofilms (Fig. 1 b). The biofilm may act as a barrier at the surface of the MP particle influencing the (kinetics of) exchange of chemicals: it was observed to stop the leaching of metallic additives from plastic, both through the analysis of metal desorption in solution (observed for example for tin and antimony in PLA and PET, respectively [57]) and by the analysis of metals directly in the plastic matrix of pristine and biotically aged MPs [84]. Beside this “cover effect”, the use of plastic as a carbon source by the biofilm community can further increase MP degradation [60], leading to higher leaching rates. These aspects need specific attention in future studies of MP biotic aging.

4. Analytical methods to assess MP aging

A wide range of analytical techniques has been used to assess the aging of MPs, depending on the different aging processes and analyzed properties. In the following paragraphs, we critically review these techniques.

4.1. Analytical characterization of abiotic aging

Mechanical and surface properties of MPs can be analyzed by a range of techniques. The static tensile strength is the most used approach to assess the changes in mechanical properties of plastic after aging: it is analyzed using a dynamometer, adding a continuous force on macroscopic plastic fragments with a specific size and a dumbbell shape [29,85]. The variation of plastic surface hydrophobicity is another technique used to assess changes in plastic surface chemistry. Hydrophobicity is typically studied through contact angle and zeta potential measurements [31]. A more detailed characterization of aspects concerning surface chemistry and physicochemical properties can instead be achieved using microscopy, spectroscopy, and thermal analyses [86]. The list of methods and analytical endpoints is given in Table 2.

Changes in the size, shape, and surface features (formation of cracks, pits, and holes due to oxidative processes and mechanical stress) of MPs can be observed by microscopy techniques, such as optical and scanning/transmission electron microscopy (SEM/TEM, Fig. 2) [31]. Electron microscopy techniques can be coupled with energy dispersive X-ray spectroscopy (EDX) to provide local semiquantitative information on the near-surface (sampling depth of few microns) elemental composition of MPs and potentially reveal the presence of additives (e.g., catalysts) in a non-destructive way [87]. Detailed morphological information can be gained also by atomic force microscopy (AFM [88]). This approach can provide topographic imaging at the nanoscale resolution, enabling morphological investigation at a nanoscopic scale and a quantitative analysis of the increase of surface roughness following aging. For instance, Aghilinasrollahabadi et al. [33] observed a four-fold increase in rugosity after 60 days of mechanical aging (from 26 nm to 108 nm, Fig. 2 e-g). Confocal laser scanning microscopy (CLSM) is applied as well: it permits micrometric scale resolution and the recognition of chemical markers (e.g., specific polymer types or adsorbed compounds)

Table 2
Physicochemical features and analytical techniques deployed for their analysis to assess the abiotic aging of MP. Examples of studies using these specific techniques are reported in “References” column.

Feature	Deployed techniques	References
Size and morphology	Optical microscopy, SEM, TEM, CLSM, AFM	[31,33,104]
Surface functional groups	FTIR, Raman spectroscopy, XPS	[29,39,42,52,85,105]
Chemical composition	Py-GC-MS, EGA-MS, LIBS, LA-ICP-MS, ToF-SIMS, SEM-EDX, STXM	[84,85,99,102,103]
Surface charge - hydrophobicity	Water contact angle, zeta potential	[44,66,105]
Surface area	BET measurements	[50,52]
Crystallinity	XRD, Raman, FTIR, DSC	[25,85,106]
Mechanical properties	Elongation tests	[29,85]
Thermal properties	TGA-DSC	[66,105,107]

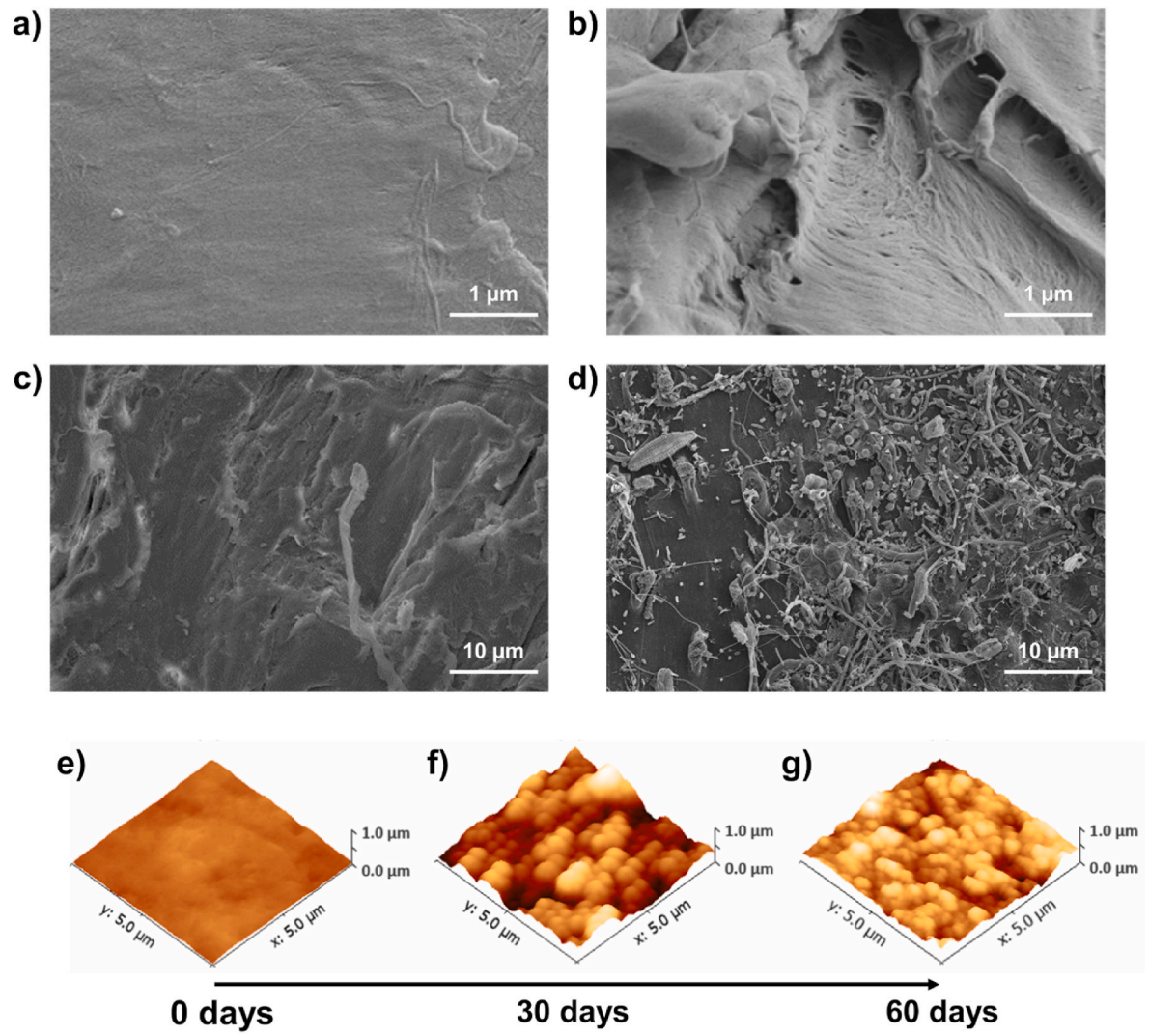

Fig. 2. Examples of microscopy applications to analyze abiotic and biotic aging on PE. a-b) SEM micrographs of pristine (a) and UV aged (b) PE fragments (adapted from Ref. [36],copyright permission from Elsevier). c-d) SEM micrographs of field aged PE samples without (c) and with (d) a developed biofilm on plastic surface (adapted from Refs. [90,91], contents under creative common license). e-g) example of AFM topography used to assess the roughness before (e) and after 30 (f) and 60 (g) days of mechanical aging with sand (adapted from Ref. [33], copyright permission from Elsevier).

through fluorescence analysis. Melo-Augustin et al., for example, recognized the polymer type and some classes of additives in plastic fragments using this technique [89]. Beyond the qualitative morphological characterization of the surface, the increase in surface area after degradation of the amorphous phase of polymers has been considered as a measurement that can correlate to the degree of aging. This can be done using the Brunauer–Emmett–Teller (BET) method based on a measure of the gas adsorption on the plastic surface [50,52].

Spectroscopy techniques, such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, are non-destructive techniques enabling the assessment of changes in surface functional groups (for example, deriving from their oxidation). These analyses are often conducted in addition to optical microscopy [10,28].

In the context of assessing the aging of MPs, it is important to obtain measurements of the differences between surface and bulk material properties, as typically aging proceeds from the surface. Attenuated total reflectance analysis using FTIR can help in highlighting surface modifications after aging. With a reduced sampling depth (usually in the range 0.5–5 µm, depending on many factors such as the quality of the sample contact with the optical crystal and its nature), this technique can yield data on the actual surface chemistry thanks to the limited interaction with the bulk, unaged, polymer matrix.

The spectra obtained by Raman and FTIR measurements can be treated to highlight specific bands typical of polymer aging. Specific band indexes are often used as they permit a quantitative assessment of the aging of the polymer matrix. These are usually presented as ratios between oxygen containing functional groups (e.g., carbonyl and hydroxyl groups) and reference peaks selected depending on the analyzed polymer [15]. Moreover, Raman and FTIR spectroscopy can give insights on both crystalline and amorphous phases of polymers and their changes induced by aging. Degree of crystallinity and crystal size can be also measured by differential scanning calorimetry (DSC) [92]. More detailed information on crystallinity can be obtained by X-ray diffraction (XRD) [93,94]. This technique, however, requires a fine powdering of samples which can introduce problems in the preparation of MP samples [95]. Additionally, XRD is highly effective in characterizing well-defined crystal structures and being less suitable for amorphous materials. Thus, a comprehensive assessment of both crystalline and amorphous regions should involve a combination of Raman or FTIR with XRD and DSC to achieve a complete picture of polymer crystallinity changes.

Information regarding the chemical composition of the outer surface (e.g., in the range of nanometers from the surface) can be achieved by X-ray photoelectron spectroscopy (XPS). The alteration of C 1s and O 1s

signals can be attributed to hydroxyl, carbonyl, and carbon-oxygen functionalities generated by the oxidation/hydrolysis-induced chain scissions [52]. This technique permits a more detailed analysis of surface oxidation (especially when induced in laboratory experiments) in comparison to FTIR measurements, since oxidation processes (and especially UV induced oxidation) primarily affect the top layer of the polymer matrix. For example, the use of XPS permitted to gain a better evaluation of the main oxygen containing groups generated after aging of PE and PS in laboratory studies, which were mainly ketones [39]. However, while being less performing than XPS, FTIR can yield sufficient information to understand polymer oxidation and is still more commonly used as a reference technique owing to its easier operation, lower costs, and higher diffusion [39].

Thermo-analytical approaches are also emerging as tools to analyze MP aging. Thermogravimetric analysis (TGA) and DSC can be used to assess changes in the thermal stability and melting behavior of MPs [96]. The combination of thermal degradation processes with gas chromatography (GC) and/or mass spectrometry (MS) analysis represents a great potential for detailed quantitative and qualitative chemical analysis of the bulk material. The most commonly adopted approach relies on pyrolysis (Py-GC-MS) at high temperatures (500–650 °C) under anoxic conditions to volatilize the polymer [24]. Volatile species separated by GC can be analyzed in MS, which has the potential for providing high resolution data on the changes in the chemical composition of the plastic during degradation [97,98]. Ainali et al. [85] reported a primer of Py-GC-MS to analyze the mechanisms of PE, PP and PS after UV aging: they observed the increase of thermal byproducts such as aldehydes, esters and carboxylic acids in aged MPs in comparison to pristine ones. Other thermo-analytical and/or mass-based methods are applied in this research area, such as evolved gas analysis-MS (EGA-MS [99]) and matrix-assisted laser desorption/ionization time-of-flight MS (MALDI--ToF-MS [100]). The latter exploits a soft ionization and can overcome the limitation of the narrow mass range of GC-MS (often insufficient to analyze high molecular weight compounds).

All thermal degradation-based strategies result, however, in the destruction of plastic samples hindering the determination of the particle size and shape. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a surface analysis technique that offers both a high molecular specificity (analysis of inorganic and organic species) and imaging capability. Thus, it can provide information on particle sizes, their composition and surface aging [69,101].

Finally, laser-based analytical techniques were recently applied in the investigation of aged MPs [84,102]. Direct approaches such as laser-induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enable the analysis of aged MPs without requiring specific pre-treatments. LIBS is useful to identify different types of plastics and major elements, whereas LA-ICP-MS is a powerful tool also to monitor the adsorption and leaching of metal traces exploiting the high sensitivity of ICP-MS [84,102]. Synchrotron-based techniques, such as scanning transmission X-ray microscopy (STXM), were also very recently probed for the analysis of aged MPs [103]: this high-resolution technique enabled the reconstruction of aging mechanisms and gave chemical insights within nanometric spatial resolution. It permitted the profiling of chemical alteration of the polymers composing plastic samples until reaching the bulk polymer matrix for different plastic types (including PE, PET and PS). However, operational costs and the need for the access to synchrotron facilities limit their broader application.

4.2. Characterization of biotic aging

The analysis of biotic aging, especially concerning surface chemical properties and morphology, partially reflects the same techniques implemented for abiotic aging [34]. For example, functional groups of biofilms present on MP fragments may be characterized using FTIR or Raman spectroscopy [108], while changes in surface charge and wettability are analyzed through zeta potential and contact angle measurements, respectively [44]. The attachment of a biofilm on MPs and its morphology may be analyzed using an optical microscope, CLSM [104] or SEM to look more closely at the shape of the microorganisms colonizing the surface of the microplastic [31,46]. The detailed analysis via SEM easily permits the recognition of organisms colonizing MPs, enabling the taxonomical definition of the community composing the biofilm (e.g., Refs. [57,91]). Elemental composition of plastic biofilms can also be achieved by EDX mapping [31]. In addition, laser based techniques (i.e., LA-ICP-MS, LIBS [84]) are also recently reported to investigate the elemental composition of biofilms on MPs.

Beyond physiochemical characterization, there are specific bioanalytical techniques to analyze the composition and physiological functioning of biofilm on MPs (Table 3). Quantification of the developed biofilm, for example, may be done by gravimetric analysis: MPs with developed biofilm are weighed before and after the biofilm is removed (e.g., by oxidation [46]). Biofilms can also be indirectly quantified by the determination of proteins as a proxy for the number of microbial cells [109]. Another approach is based on a staining technique using crystal violet dye: the dye is used to stain the cellular nuclei of organisms composing the biofilm and the concentration of the extracted dyes, characterized for example through colorimetry, is linked to the amount of the extracted biofilm [109,110].

For MPs aged in water, as well as on the surface of soils or sediments, biofilm development can be monitored by measuring photosynthetic pigment content [46,111], but this is obviously not relevant for samples aged in deep soil or wastewater without sunlight [84]. In contrast, the content of EPS can represent a useful approach for the determination of biofilms. EPS are typical of prokaryotes, but are also found in some fungi and algae, and play an important role in the attachment of microorganisms on substrates, including MP surfaces. To reveal the microbial composition of the developed biofilm, DNA sequencing can be used [34,108,112,113], while the microbial activity of the biofilm can be measured via activities of various enzymes. For example, Miao et al. [114] followed the oxidizing capacity of microorganisms in a biofilm toward various carbon sources, while Rozman et al. [46] determined the activity of ureases as they are commonly found enzymes in many microorganisms.

5. Analytical implications of MP aging

Abiotic and biotic aging processes affect all MPs in the environment to some degree. This can have potential important implications not only for their environmental behavior, but on their behavior during analysis. These implications can complicate MP accurate detection and quantification in environmental samples, especially given that particles may represent a wide range of alterations induced by different aging processes prior to sampling. Since analytical methods for MPs are often developed and validated using pristine reference MP materials, this potential problem has, thus far, been poorly considered. The changes in surface chemistry and mechanical properties induced by aging may affect the whole analytical workflow for the extraction, clean-up and quantification of MPs in samples (which usually include at least a density separation and a digestion of organic matter prior to the actual analysis, Fig. 3) in an unpredictable way. These issues should be carefully considered both in the setup of new analytical methods and when assessing quality assurance/quality control protocols and harmonization strategies (e.g., to create reference materials [115]).

5.1. Potential problems related to extractions and pre-treatments

Sample purification and extraction of MPs is a process extensively used in research and monitoring, especially when determining MP content in complex matrices such as soils, sediments, and biological samples. This normally includes, at least, a density separation step (essentially to remove inorganic particles using concentrated salt

Table 3
Highlights of advantages and drawbacks of the different available analytical techniques to analyze biotic aging.

Analytical technique	Analyzed feature	Advantages	Drawbacks
FTIR and Raman spectroscopy	Surface functional groups	Permits to recognize the main components of biofilm and polymer matrix Can be coupled with optical microscopy	Requires abundant data handling
Optical microscopy	Morphology	Easy to operate Cost-effective	Limited information
CLSM	Morphology, chemical features and taxonomy	Permits to use chemical markers Generates high-resolution 3D images	Higher cost than optical microscopy
SEM-EDX	Morphology, taxonomy and chemical features	High-resolution of morphology Can couple morphological features and chemical composition of the sample	More expensive than other microscopy techniques Requires sample fixation and pretreatment (e.g., metal sputtering)
Laser based techniques	Morphology and chemical features	High sensitivity Can be coupled with optical microscopy	Based on elemental markers Limitedly used Costly
Gravimetric analysis	Biomass of biofilms	Permits a quantitative assessment of biomass	Destructive technique (requires the digestion of biofilms)
Determination of proteins or nuclei via spectroscopy	Biomass of biofilms	Easy to perform Frequently used in biology	Permits only a semi-quantitative (relative) assessment of biomass in the biofilm
Analysis of photosynthetic pigments	Biomass of biofilms	Quick and non-destructive fluorescence analysis Easy to perform	Limited to photosynthetic organisms and photic environments
Analysis of EPS	Biomass of biofilms and functioning	Easy to perform Gives information on biofilm functioning	Permits only a semi-quantitative (relative) assessment of biomass in the biofilm EPS production is dependent on the organisms composing the biofilms
DNA analysis	Taxonomy and functioning	High resolution technique Provides information on taxonomy and enzymatic functioning	Costly Requires abundant data handling

solutions) and one or more chemical (or enzymatic) digestion steps that remove excesses of organic matter in the sample [116–119].

First, the enhanced embrittlement of aged MPs can easily induce fragmentation of MPs during the whole analytical protocol, leading to potential artifacts in the measurement. Namely, the chemical treatment or mechanical abrasion induced by sample processing steps may result in the generation of more particles, particularly affecting analyses that result in count-based concentration data. This may also reduce formerly larger particles to smaller fragments that are smaller than the pore sizes of meshes, screens, or filters that are commonly used in sample processing protocols.

Aged MPs can also present specific challenges for an effective density separation. Biofouling is known to affect particle density and some issues in the process of density separation have been already highlighted: for instance, Halbach et al. [120] found changes in recovery rates for density separation step after incubation for biofouling on some polymers in a simulated seawater algal community inoculum. Similar problems can obviously emerge also for MP aged in soils or sediments. Another potential issue related to the density separation of aged MPs (both biotically and abiotically), is the different sedimentation rate and hydrophilicity (e.g., Ref. [18]). These issues were not assessed yet to the best of our knowledge considering MP extraction and will need specific investigations.

Digestion processes are already known to potentially affect different pristine MPs and can have more serious analytical implications for aged environmental ones [121–123]. As a matter of fact, the reagents used for the removal of organic matter are the same used to simulate abiotic polymer oxidation and hydrolysis (such as H_2O_2, HNO_3 and NaOH). These reagents, when applied on environmentally aged polymers, may even more easily create artifacts and complicate the analysis of MPs. MP fragmentation can easily be enhanced during the digestion, altering the analyzed particle size distribution. For example, a 0.25 M potassium hydroxide (KOH) treatment with sonication for 15 h on 1 cm^2 square-shaped fragments showed the generation of up to 10^5 particles in unweathered PLA, PET, and PS [124]. While the processes used for organic matter digestion are often performed under milder treatment conditions than those reported in this study, the increased brittleness of aged MPs compared to pristine polymers may lead to increased fragmentation. In any case, specific investigation into the recoveries of pristine and aged MPs at different grade of aging is necessary to understand the potential of chemical treatments for inhibiting accurate detection and quantification in the final analysis. Similarly, different reagents for MP digestion protocols are known to affect the weight and shape of pristine MPs [117]: this effect can be accentuated in aged MPs. A recent study by Lessa Belone et al. [125] highlighted that abiotically aged MPs composed of different polymers had a higher surface rugosity and fragmentation after a digestion with H_2O_2 at 40 °C for 24h. In addition, they observed a decrease in mass of up to 5 % after digestion. These issues may cause under- or overestimation of MP fragments, depending on the size of particles generated and the size detection limits of the techniques used for further counting [86,126].

On the other hand, other studies have reported limited issues in digestion procedures when validating their methods using MP particles obtained by environmentally aged samples. For example, a “gentle” digestion of mussels with an enzymatic protocol did not degrade environmentally-collected fragments of low density PE, PP, and expanded PS [127]. Similarly, a study reported the ability to recognize PE fragments in an organic rich sample after digestion with Fenton’s reagent [22]. A more systematic validation of the recovering of different MP typologies affected by different degrees of aging is needed to confirm these observations and highlight more specifically the conditions where analytical results may be affected.

5.2. Potential problems related to analysis

Both abiotic and biotic aging have implications for the effectiveness of particle detection and quantification, and the determination of chemical composition.

Polymer embrittlement driven by abiotic aging can have negative implications for size analysis and enumeration (as stated in Section 5.1). Namely, particle fragmentation induced by sample processing treatments may transform particles that were previously above the size detection limit for a given instrument or analysis into particles that now fall below this threshold, resulting in an underestimation of concentrations by techniques that yield count-based data (such as FTIR or Raman

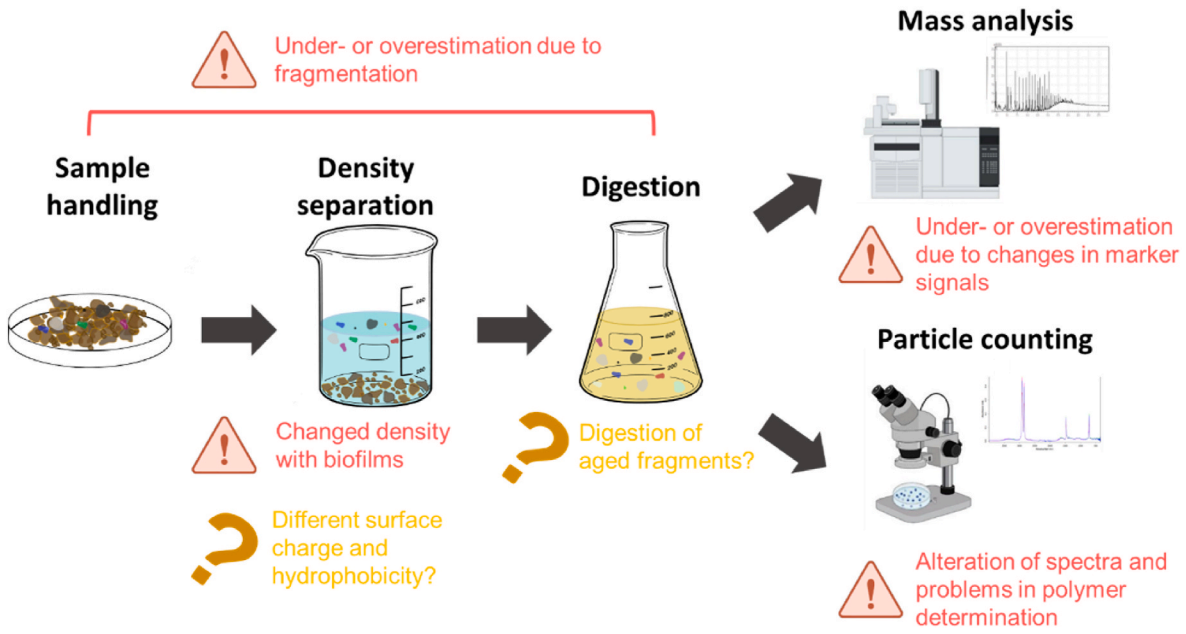

Fig. 3. Scheme of workflow for MPs extraction and analysis from complex media (e.g., a soil sample) and potential issues for the analysis of environmentally aged MPs. Critical steps likely to affect results are highlighted in red, while possible issues affecting the measures and requiring further investigation are indicated in yellow.

spectroscopy). Beside the issues in the counting of particles, also the particle determination by spectroscopic techniques can be affected by abiotic aging: a loss of spectral information is induced by changes in surface groups and increased rugosity [126]. The problems in polymer determination can be more marked when a preliminary digestion step is applied to remove organic matter: altered FTIR signals are in fact observed with pristine MPs after several digestions steps for organic matter removal on PP and PE [23].

Biotic aging presents also several implications for the chemical characterization of MPs via optical and spectroscopic methods, as the constituents of biofilms on the surface of MPs can interfere with the analysis [88]. For example, the high fluorescence of algae within the biofilm may interfere with the use of Raman spectroscopy for chemical characterization of MPs [84] or some constituents of biofilm can be indicated as new functional groups in spectra provided by FTIR analysis: this effect may cause the loss of spectral information needed to recognize specific bands of plastic polymers [128]. To date, no generalized functions have been developed to correct for this matrix effect and aid in consistent determination. On the other hand, a more thorough removal of organic matter to avoid such a complication can affect the quality of the analysis and introduce artifacts (as discussed above).

Chemical changes induced by abiotic aging can negatively impact the chemical characterization of MP by mass spectrometry as well. For example, samples of PE, PS, and PP showed altered chemical markers in their mass-chromatograms using double shot Py-GC/MS [85,98]. Most studies use virgin polymers as standards for calibration, and the change in peak height or area of the selected pyrolysis markers for quantification compared to aged polymers will lead to over- or underestimation of the polymers present. Thus, performing Py-GC/MS on environmental samples without knowing the effect of aging on the polymers is challenging. Available literature treating this issue only covers a few polymer types and is also limited in the morphology size and chemical content of the material tested.

The effect of biotic aging on the analytical assessment of MPs via Py-GC-MS is still to be understood. To the best of our knowledge, it is not yet known to what extent biofilms present on plastic particles influence the identification and quantification of polymers. While, hypothetically, this issue should only affect the quantification via Py-GC-MS to a limited degree (owing to the well distinct chemical composition of biomass by-products after pyrolysis; e.g., Ref. [129]) this speculation should be validated by evidence. In summary, there is a clear need to consolidate knowledge in this specific area to fully empower Py-GC/MS as a main and reliable analytical tool for MP research.

6. Ways forward and recommendations

The issues highlighted in this review showed the need to better understand and, possibly, overcome analytical issues related to the analysis of MPs aged in the environment, especially in soils where photooxidative, biotic, and mechanic aging processes may take place simultaneously. In this chapter we will suggest the possible strategies to overcome some of these issues and we suggest the next steps toward the creation of realistic aged MP reference materials at increasing environmental relevance.

6.1. Toward the creation of aged MP reference materials

An important improvement to overcome issues in the analytical assessment of environmental MPs could be introduced by the use of adequate aged reference materials during both validation, calibration (e.g., for Py-GC-MS analysis), and for recovery tests (setting up extraction and purification methods) [21,90]. Some effort has been placed toward the creation of MP reference materials (see e.g., Refs. [44,130]). However, the integration of aging processes in this process is still largely overlooked.

A key issue for the generation of aged reference materials stands in the harmonization of aging protocols. This is fundamental also for the comparison of findings among studies testing aging processes. For example, considering a common practice such as UV aging, we encourage the detailed description of the UV source (e.g., emitting spectrum and irradiance) and its comparison with the potential equivalence of natural light radiation [29]. We also encourage comparative studies of UV aging conditions and comparison of results with other physicochemical stressors [35].

Another important step toward the creation of realistic aged reference materials is the use of MPs that can be obtained with consistent and

known chemical formulations. Additive chemicals are in fact commonly added to plastic products and their presence obviously affects physico-chemical properties and polymer aging processes [30,44]. We also suggest incorporating biodegradable polymers in studies assessing the effects of biotic and abiotic aging. Considering their emerging and increasing abundance, these polymers will need to be included as references materials for MP analysis [53].

6.2. Improving environmental relevance in the simulation of MP aging

Beyond the harmonization of aging simulations, the creation of appropriate reference materials requires to realistically mimicking natural aging processes. It is therefore of the upmost importance to recreate the relevant aging pathways more likely to affect MP proprieties in specific environments [26]. To do so, we suggest to compare different biotic and abiotic aging processes at a time through multi-tiered, laboratory-based experiments [31,63]: this approach permits the ranking effects of different aging processes, as well as testing potential synergistic or antagonistic effects of multiple aging processes at a time, ensuring improved environmental relevance while still permitting tunable and controllable conditions. As an example, the "cover effect" of biofilms on MPs in mediating the chemical properties of its surface (see section 3.1) needs further specific investigation, such as the design of simulated aging processes (e.g., though UV irradiation) before and after the formation of a biofilm on MPs. We also suggest comparing different laboratory- and field-based approaches (e.g., Refs. [25,105,106]), or at least the comparison of simulated aged MPs with environmental samples, to test the relevance of the former.

6.3. Alternative analytical approaches for aged MP analyses

Finally, we suggest other potential analytical alternatives to overcome the analytical issues generated by MP aging. Specific data treatment techniques may overcome some problems induced by aging of plastic; for example, the use of multivariate statistics to classify polymers via FTIR spectroscopy gained satisfying results also using environmentally aged materials [131]. We also suggest exploring the use of direct analytical techniques (e.g., LIBS, LA-ICP-MS, ToF-SIMS) to enable the analysis of MPs that avoids the need for pre-treatments that may induce loss or fragmentation of MPs (e.g., removal of organic matter by digestion). However, the application of these techniques for the analysis of MPs relies on the analysis of chemical markers (e.g., some metallic elements for LIBS and LA-ICP-MS [5,84]) which can be very variable in environmental samples. This hampers their further exploitation in the analysis of environmental MPs.

7. Outlook and conclusions

In this review we highlighted the key role of environmental aging of MPs, with a focus on soil and freshwater environments, highlighting both the environmental consequences and the expected implications for their analytical assessment. We showed the current strategies and future steps to simulate environmental aging, highlighting the need for laboratory-based approaches to elucidate the effects of different abiotic and biotic factors in changing the physicochemical proprieties of aged MPs. We also highlighted the current needs to successfully address the environmental implications of MP biotic and abiotic aging (alone and in combination) for the degradation and embrittlement of plastic polymers and the leaching of potentially toxic chemicals from their matrix. We then assessed, for the first time, the potential implications of aging during the analysis of MPs from environmental samples, especially from challenging matrices such as soils. This issue is generally overlooked when calibrating and setting up new protocols. Several critical aspects to be taken into consideration when handling, extracting and analyzing these samples were described here.

CRediT authorship contribution statement

Gilberto Binda: Funding acquisition, Visualization, Writing – original draft. **Gabriela Kalčíková:** Writing – original draft, Writing – review & editing. **Ian John Allan:** Writing – review & editing. **Rachel Hurley:** Writing – review & editing. **Elisabeth Rødland:** Writing – review & editing. **Davide Spanu:** Writing – original draft, Writing – review & editing. **Luca Nizzetto:** Supervision, Writing – review & editing.

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.

Data availability

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

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