Nanoplastics in the Environment

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ABSTRACT

There has been an increasing awareness of the potential ecotoxicological consequences of the growing presence of plastic materials in the environment. Among these, due to their inherent physical and chemical characteristics, microplastics have received special attention, though smaller particles, defined as nanoplastics, could have more pervasive effects. However, their presence is difficult to be accurately determined, due to the technical difficulties in isolating and quantifying these small particles. There is, nonetheless, an ample consensus that nanoplastics are not only present, but that they also pose a significant threat to the environment, organisms and, ultimately, human health, not only due to their reduced size (<1 μm), but also due to their characteristic high surface area, which may have ecotoxicological implications, as other contaminants, including organic pollutants, may be adsorbed. In spite of these potential harmful effects, currently available data should be examined carefully, as most studies have been based on the use of nanoplastics and/or organic pollutants whose concentrations far exceed those expected in the natural environment. Herein, based on the currently available literature, the most relevant sources and fates of nanoplastics are discussed, as well as their potential – if any – effects and the key challenges scientists currently face in this field of research.

1 Introduction

Plastics are highly malleable materials that can be molded into solid objects of virtually endless shapes and sizes. The International Union of Pure and Applied Chemistry (IUPAC) defines plastics as a broad term describing any "polymeric material that may contain other substances to improve performance and/or reduce costs".[1] Although these may be semi-synthetic organics, plastics are typically synthetic polymers, mostly derived from petrochemicals.[2] Exhibiting high molecular mass and plasticity, these materials are easy and cheap to manufacture, which, coupled to their water, chemical, thermal and water and light resistance, has rendered plastics ubiquitous with unquestionable societal benefits and can presently be found from stationary items to spaceships.[3]

The large-scale production of plastics, initiated in the 1950s, surpassed the 320 million ton mark in 2015,[4] and the success of these materials has proved versatile in many forms, including natural polymers and modified natural polymers, thermoplastics and, due to increasing environmental awareness, biodegradable plastics.[2,5] This subsequent widespread use of plastics, highly resistant to degradation, has resulted in the accumulation of vast amounts of plastic waste across the globe. This accumulation stems from the inherent paradox that is at the basis of the development of plastics: cheap, flexible, **resistant to degradation** materials designed to be **disposable**. In fact, over 40% of all plastic items produced annually are designated for packaging,[4] that is, for immediate discard, and plastics constitute up to 10% of all solid municipal waste worldwide.[6] Interestingly, although plastic sources are mostly terrestrial, some estimates have pointed that up to 80% of all generated plastic waste ends up in the Oceans.[7] This movement of plastic waste from economy to the environment has been described by Newman and colleagues[8] and is summarized in Figure 1. The accumulation of marine plastic litter can, hence, be attributed to market failure, meaning that the price of plastic products does not reflect the true cost of treatment and/or disposal. In other words, the cost of either recycling or disposal, deliberate or accidental, is not borne by producers or consumers, but rather by society.[8]

Additionally, due to the fact that these debris can travel across large distances, as the result of the concerted action of wind, tides, currents and even maritime traffic, with inherently highly complex mechanisms,[9] it has long been recognized that sources and sinks of plastic debris may be highly spatially dispersed[10] and that, subsequently, local solutions are inadequate and insufficient. Therefore, such global distribution of plastics, including in remote and isolated areas, such as the benthos,[11] arctic[12] and antarctic[13] regions has raised the alarm towards the potential risks that these materials pose to the environment, and, ultimately, to human health, as reflected by the increasing attention paid not only by researchers, but media and the general public as well. Such notoriety has been especially evident for microplastics, plastic particles that are less than 5 mm. Less attention, however, has been paid to nanoplastics, which are of particular concern as,
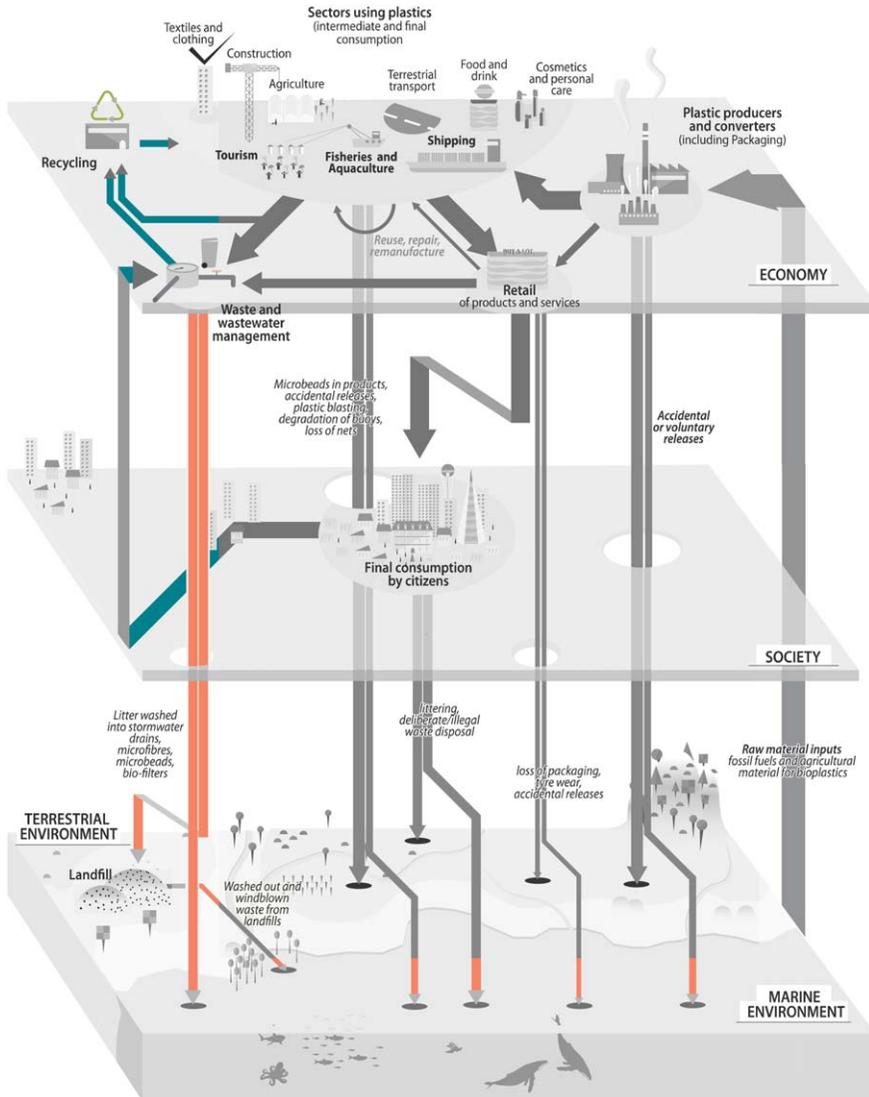
Figure 1 The movement of plastic waste from the economy to the environment. Image credit: GRID-Arendal and Maphoto/Riccardo Pravettoni, available at https://www.grida.no/resources/6908.

owing to their reduced size, may not only be ingested by small organisms at the base of different food-webs, but can also potentially pass biological membranes and thus affect organisms at a cellular level, including the functioning of blood cells and photosynthesis.[2,14] These dangers are further exacerbated by the increased surface-area-to-volume ratio, when compared to microplastics, which have been demonstrated to result in the adsorption of highly toxic substances onto the surface of these materials.[15,16] It hence

becomes of the utmost importance to understand the sources, fates and behavior of nanoplastics in the environment, as well as the potential consequences for biomes.

2 Defining Nanoplastics and Ascertaining Their Sources

First, it is necessary to define what constitutes a ''nanoplastic''. Nano-particles exhibit specific properties that differ from their bulk counterparts and are generally considered as particles with less than 100 nm in at least one dimension.[17] However, for nanoplastics, a clear consensus classification has not yet been reached and multiple size-based definitions have been proposed.[18] For example, Browne *et al.*,[19] da Costa *et al.*[2] and Hartmann *et al.*[20] have suggested defining nanoplastics as particles less than 1 μm, while others, such as Mattsson *et al.*[21] and Koelmans *et al.*[18] have proposed the already used definition for engineered nanomaterials, that is, particles less than 100 nm. Interestingly, however, Koelmans and co-workers have since adopted the increasingly accepted size cutoff of 1 μm.[22] Other authors have suggested different thresholds, such as 20 μm, as proposed by Wagner *et al.*[23] Although such discussions may be considered merely semantic in nature, they have a profound effect in both the research and development and implementation of regulations, directives and guidelines. Hence, al-though the use of the size definition in place for non-polymeric materials – less than 100 nm – may seem logical from a practical point-of-view, as it minimizes confusion within the field of nano-environmental health and safety and may benefit from the existing regulatory mechanisms in place for engineered nanomaterials, it fails to encompass the environmental inter-actions, implications and impacts of slightly larger particles within biomes at a more biologically significant level. In fact, this is at the core of the proposed 20 μm threshold proposed by Wagner,[23] as this is the categoriza-tion used by ecologists to classify plankton as nanoplankton.[24] Therefore, defining nanoplastics as particles less than 1 μm may be reasoned, as this may be construed as the size at which these particles have a *de facto* impact from a biological and environmental perspective, because, although nano-plastics are the least known type of plastic waste, they are also, potentially, the most hazardous.[18]

Nanoplastics may occur in the environment as a result of their direct re-lease or from the fragmentation of larger particles. They may, similarly to microplastics,[25] therefore be classified as either primary or secondary na-noplastics. The former stem from the direct release from applications and/or products in which these polymeric materials are used or formed.[18] Cosmetic products, paints, tires, adhesives and electronics have all been reported as sources of nanoplastics directly released into the environment,[2,18,26,27] as have industrial activities, such as the thermal cutting of polystyrene (PS)[28] and polyvinylchloride (PVC).[29] Increasingly affordable, the mass use of 3D printing has also been shown to result in the release of nanoplastics.[30] Moreover, micro- and nanoplastics may be directly transferred to the

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atmosphere due to the drying of clothes, disintegration of agricultural polyethylene (PE) foils and contaminated sewage sludge, used as fertilizer.[31] All these tend to accumulate mostly in oceans, and, as recently estimated by Jambeck and co-workers, up to 80% of all plastic found in the oceans comes from land-based sources,[32] of which nearly 94% accumulates on the ocean floor, reaching an estimated average of 70 kilograms of plastic per square kilometer of sea bed.[33] Figure 2 highlights the processes through which most of these materials accumulate in the Ocean.

Secondary nanoplastics, in turn, result from the breakdown of larger plastic particles, such as microplastics. Although the exact mechanism through which this may take place is unclear and notwithstanding the little information currently available regarding the prevalence of nanoplastics in the environment, it has been experimentally demonstrated that bulk PS, in the form of disposable coffee cup lids, could be weathered into nano-plastic particles with an average size of 224 nm in less than 60 days,[34] as the result of the concerted action of UV-radiation, mechanical abrasion and thermo-oxidation, as well as hydrolysis.

Anthropogenic in nature, plastic sources are mostly in land. However, because many plastic particles are found in sewage and treated effluents, these materials tend to accumulate in aquatic systems.[35] Additionally, despite some reports detailing the efficient removal of micro-sized plastics from wastewaters,[36] others have highlighted that this depends on the types of treatment processes available, as the inefficient removal of these materials has also been described for other facilities.[37] Such studies, however, focused on microplastics and, for nanoplastics, it is conceivable that current wastewater treatment processes may not remove these particles efficiently.

3 Fate of Nanoplastics

Determining the fate of nanoplastics in the environment is inherently difficult due to the size of these particles,[2] evidenced by the current lack of methodologies specifically aimed at the quantification of nanoplastics in environmental samples. However, it may be possible to extrapolate their fate from that of larger particles, such as micro- and mesoplastics.[18] As a significant proportion of these plastic debris occur in the oceans,[7,21] circulation models have been developed, suggesting that these materials tend to accumulate in all five sub-tropical ocean gyres,[38] and microplastics, for example, have been detected across the globe, from the Arctic[12] to Antarctic waters,[13] and throughout the water column,[39] from the surface[40] to the benthos.[41] It therefore becomes increasingly complicated to accurately determine the prevalence of these small particles in the environment. Although it has been argued[18] that mathematical models aimed at assessing the fate of nano-materials in the environment may be applied to nanoplastics (for examples, see ref. 42–44), these fail to include properties and processes that affect polymeric materials distinctively from those affecting the fate of engineered nanomaterials in the environment, namely, densities, biodegradation,
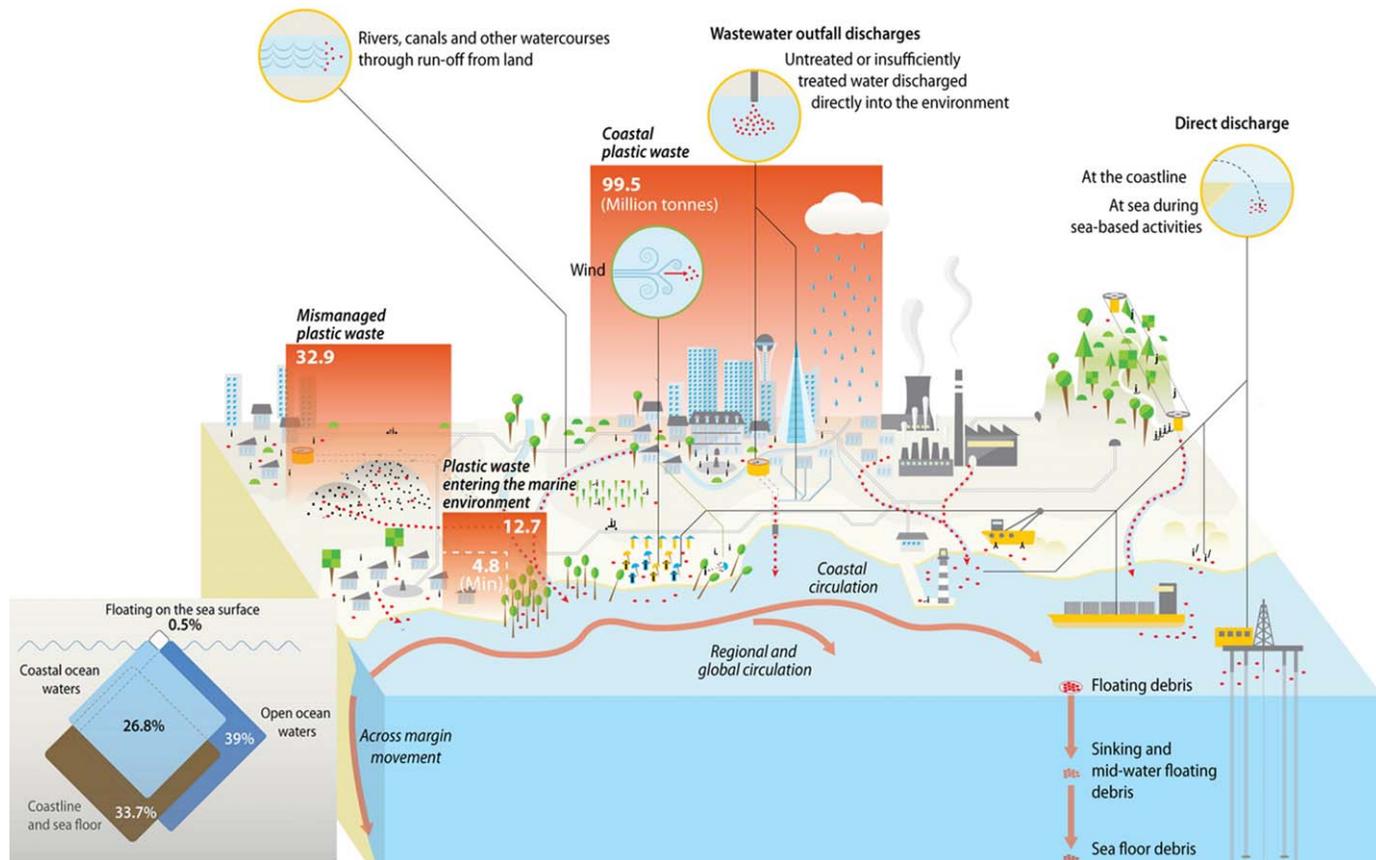
Figure 2 The pathways and fluxes of plastics into the oceans and estimated distribution of marine plastic litter in the marine environment. Image credit: GRID-Arendal and Maphoto/Riccardo Pravettoni, available at https://www.grida.no/resources/6921.

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biofilm formation, advective transport, sedimentation and re-suspension, as well as hetero- and homoaggregation. Based on a model developed for the spatiotemporal study of the fate of engineered nanoparticles in rivers,[45] an attempt was made to specifically assess the fate of nanoplastics in the riverine environment.[46] However, such modeling was based on the premise that aggregation with suspended solids ensuing sedimentation is the most probable removal process. Heteroaggregation is highly affected by the attachment efficiency between particles, which is a parameter that, presently, remains unknown for both micro- and nanoplastics and that appears to depend strongly on the polymer type.[47] Nonetheless, these are initial approaches that may bear fruit in the long term and that clearly depict the necessary avenues of research for the determination of the fate of micro- and nanoplastics in the (aquatic) environment.

For terrestrial environments, the currently available information pertaining to micro- and nanoplastics is even scarcer than that concerning aquatic environments. This may be due to numerous causes, ranging from technological limitations to prospective impacts of potential scientific findings. For example, some authors have alluded to an apparent separation between marine and terrestrial ecological research that prevents the propagation of ideas and findings from one domain to another.[48] There are also experimental hurdles currently limiting the research on terrestrial environments, as sampling, isolation and analysis of plastic particles from aquatic samples is considerably simpler than in complex organic and mineral soil matrices. Additionally, because most of the plastic consumed tends to accumulate in the ocean, as previously noted, there is an understandable prioritization of this milieu, although it should be noted that the concomitant accumulation of plastic along shorelines makes these a specific subject of research, as there is no parallel in terrestrial systems.[37,49,50]

Once in the environment, plastics are susceptible to degradation through abiotic and/or biotic processes.[51] The former constitutes an essential initial step in the degradation of the polymeric materials, as the end result is the loss of both structural and mechanical properties, yielding increased surface area-to-volume ratios, thus potentiating both microbial colonization and physicochemical interactions.[52] These mechanisms include thermal,[53] chemical,[54] mechanical[55] and photo-degradation,[56] extensively described elsewhere[52,57,58] and of which the latter is generally considered to be the most efficient degradation route occurring naturally in the environment.[2,57]

Briefly, in aquatic environments, mechanical degradation processes are enhanced by the concerted action of waves, winds and currents, which promote attrition with sand and other sediments and debris. Buoyant plastic materials, due to higher exposure to UV radiation, higher temperatures and the atmosphere,[51] endure significant chemical changes that are less prevalent in deeper waters, due to lower levels of sunlight, oxygen and lower temperatures.[59] In these environments, namely, the benthos, the reduced biodiversity, but, more importantly,[2] the reduced densities of existing microbial communities, also render biotic degradation processes negligible,[51,59] resulting in

continuously smaller particles that accumulate on the seabed and that constitute a permanent source of environmental exposure.

Regarding the abiotic pathways of degradation of polymeric materials, these can be separated into two distinct mechanisms that depend on the polymer type, namely, whether these consist solely of a C–C backbone (polypropylene (PP), PS, PVC and PE) or whether they exhibit heteroatoms in the backbone (poly(ethylene terephthalate) (PET) and polyurethane (PU)), which, according to the latest available figures, account for more than 90% of the plastics global demand.[4] Figures 3 and 4 describe the abiotic degradation mechanisms of plastics with a carbon–carbon backbone and with plastics with heteroatoms in their backbone, respectively, in the marine environment, as described by Gewert and co-workers.[54]
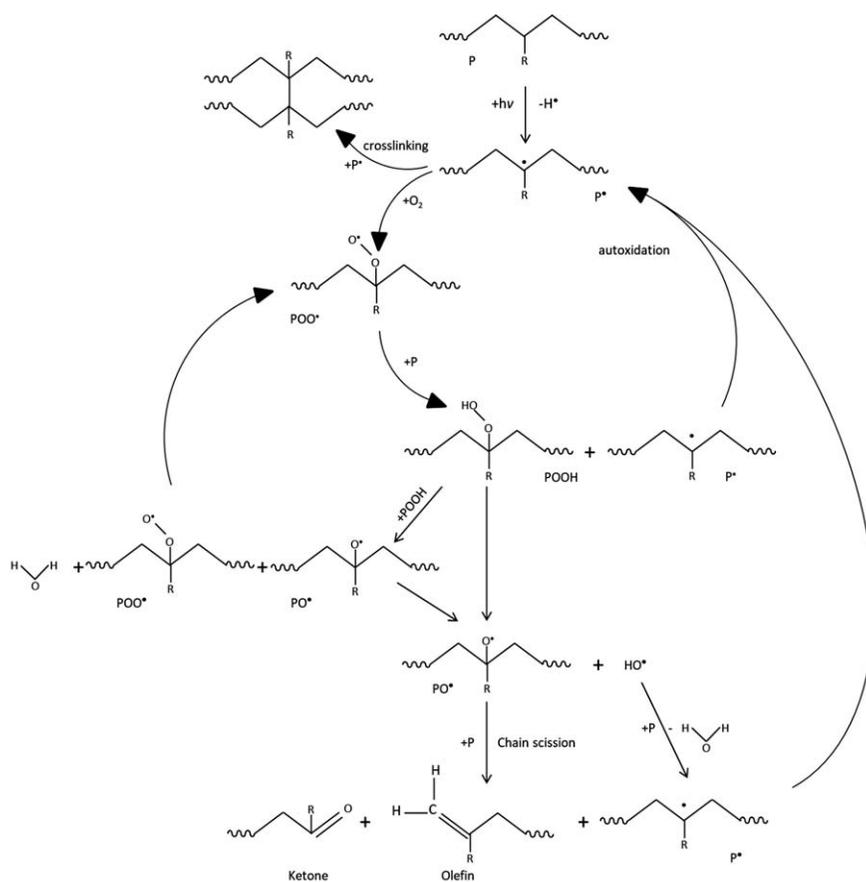
Figure 3 Abiotic degradation pathways of plastics with a carbon–carbon backbone following initiation by photolytic cleavage of a C–H bond on the polymer backbone (P = polymer backbone). For PE, R = H; for PP, R = CH_3 and for PS, R = aromatic ring.
Adapted from ref. 54 with permission from the Royal Society of Chemistry.
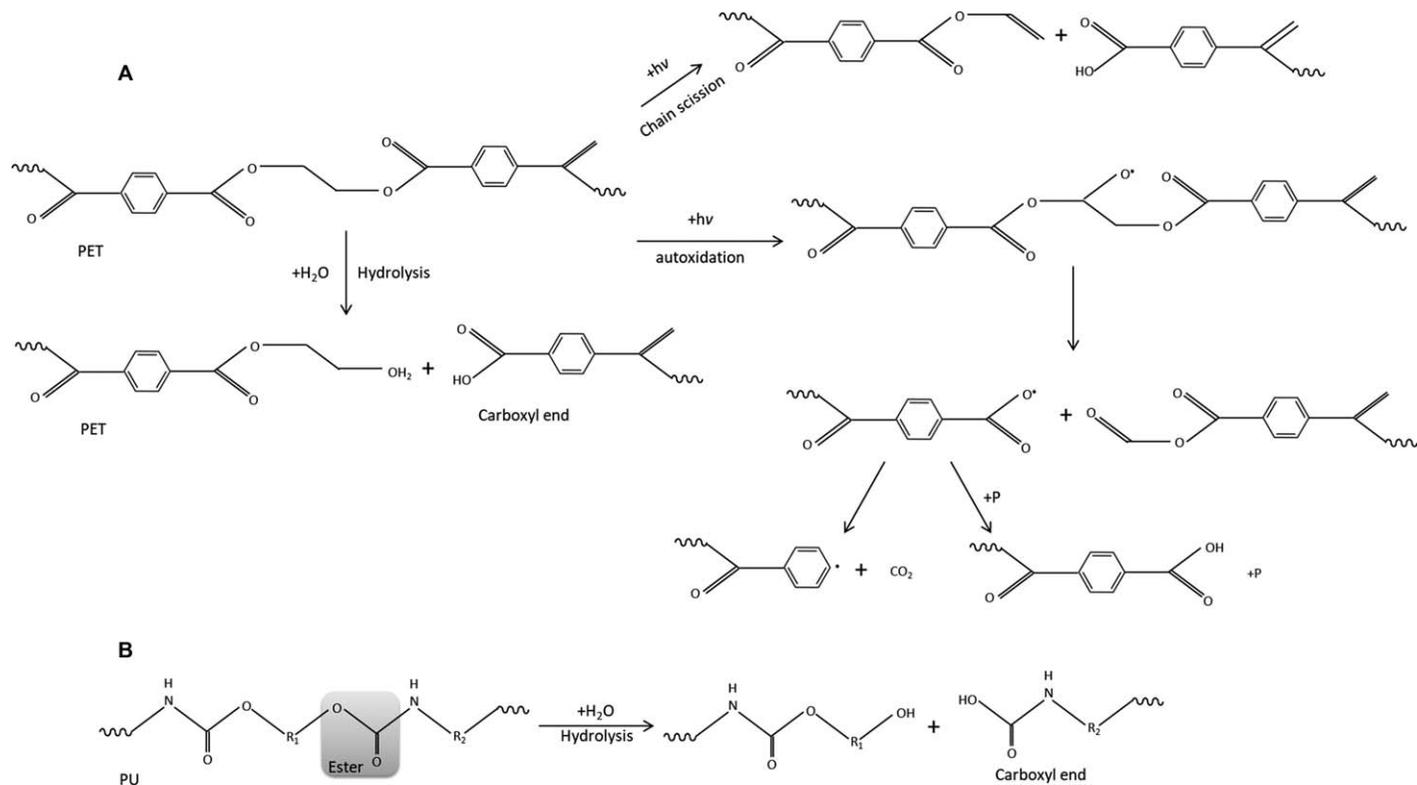
Figure 4 Abiotic degradation pathways of plastics with heteroatoms in their carbon backbone. (A) The abiotic degradation of PET and (B) the hydrolytic degradation of the ester bond of PU.
Adapted from ref. 54 with permission from the Royal Society of Chemistry.

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Considering the described pathways of degradation, for PS, PP, PS and PVC, polymers that consist of a carbon backbone, abiotic degradation precedes biodegradation, as the abiotic processes result in products of lower molecular weight, which are susceptible to biodegradation processes,[25,60,61] not only in aquatic environments, but also in soils.[62]

PET and PU, which contain heteroatoms in their main chain, may undergo photo-oxidation and hydrolysis, as well as biodegradation.[54] The subsequently formed smaller fragments and carboxylic end-groups can then undergo further biodegradation pathways, which may occur simultaneously, as, within aquatic settings, multiple factors may initiate degradation and the resulting products may be more diversified than those assumed for any given specific route of degradation. Consequently, such polymeric materials, namely, PU, have been long and widely recognized as particularly susceptible to biodegradation, whether within aquatic or terrestrial environments.[52,63–65]

However, as noted by Gewert and co-workers,[54] polymers are rarely used, and, hence, occur in the environment in their pure form. Therefore, the previously described pathways may be incomplete and the released products may include other compounds, namely, additives, during the (bio)-degradation of plastics. As noted in Figure 5, multiple factors influence the degradation of plastics, including the presence, type and quantities of such additives, thus hindering an adequate quantitative statement concerning the degradation rates of different polymers when in the environment.

There are, nonetheless, other factors that directly influence the fate of polymers, particularly in aquatic environments. The density of the polymers,
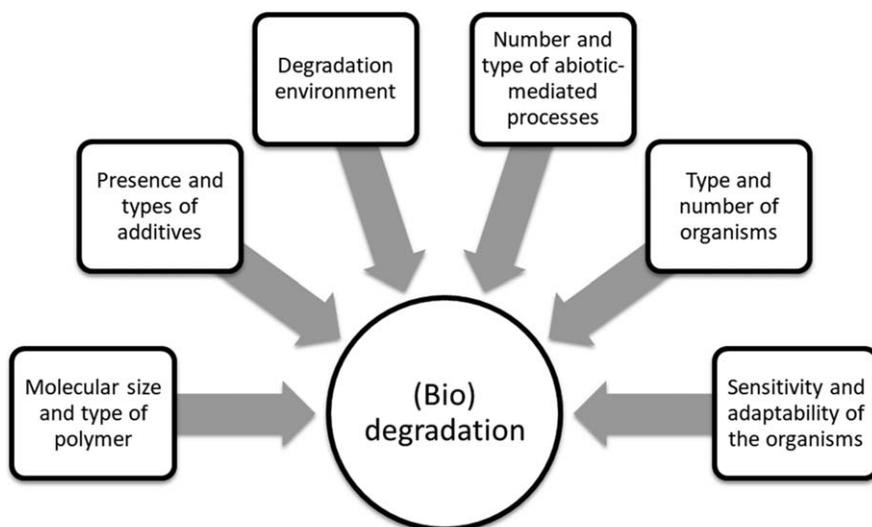
Figure 5 Main factors affecting the (bio)degradation of polymers in the environment.

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for example, determines their initial bioavailability in the water column, although these can change over time, due to phenomena such as hetero- and homoaggregation, as well as colonization by different organisms.[2] Consequently, the type of plastics ingested by organisms may vary depending on their occurrence in the water column.

In less deep waters, diverse and numerous communities of microorganisms exist, including heterotrophs and symbionts, which have been described as colonizing the surface of plastic marine debris, playing an active role in the (bio)degradation of these polymeric materials.[66]

The biological processes of polymer degradation commonly initiate outside of the cells,[2,67] which may be attributable to enzymatic action,[51] leading to a cleavage of the main polymeric chain through hydrolytic pathways,[68] independent of the milieu.[69] Utilizable groups are then formed, contributing to the continuous degradation of the polymeric materials,[51,70] sometimes involving, to different extents, both abiotic and biotic processes of degradation. Ultimately, water-soluble oligomers and monomers are generated, eventually culminating in mineralization, as they can be assimilated by microorganisms, due to being transported across the semi-permeable outer membrane and then assimilated as a carbon or nitrogen source *via* different metabolic pathways.[2] For example, PE, has been shown a degree of bioassimilation, under composting conditions, of at least 60%.[71]

In the particular case of terrestrial environments, it has been demonstrated that the type of soil is a key factor in the degradation of polymeric materials. For example, polycaprolactone (PCL) was exposed to clayey and sandy soils and results evidenced that PCL degraded to a greater extent in the former, clearly highlighting that soil texture affects the mineralization kinetics of plastics.[72] This may be due to higher moisture and organic matter contents in clayey soils. Additionally, pre-exposure to UV radiation appears to be an important factor influencing rates of biodegradation, both in soils and in the aquatic environments,[73,74] although recent works have described high rates of biodegradation of PE in artificial seawater by a marine fungus with no reported initiation with UV radiation.[61] In spite of this rather limited body of research on the fate of micro- and nanoplastics in soils, some authors have reasonably argued that some of the principles for aquatic environments apply, as many organisms present in terrestrial environments, explicitly, microorganisms, are fundamentally aquatic, as they thrive in the thin film of water that covers soil surfaces.[48] However, the presence of these particles in terrestrial environments will undoubtedly contribute to alterations in the overall composition of soils, which may entail environmental and ecotoxicological implications.

Recently, there have been attempts at developing new, more readily biodegradable polymers, whose properties – physical, optical and mechanical – can be designed and that may exhibit characteristics comparable to those of the traditional polymers, such as PET or PS.[2,75] These ''biopolymers'' can be polyesters or starch-based polymers. The former include PCL and polylactic acid (PLA), widely considered as one of the most promising biopolymers,

owing to its high transparency, molecular weight and water solubility resistance, rendering this polymer highly versatile.[76] The latter, starch-based polymers, are produced through the combination of commercial polymers with different percentages (10, 50 and 90%) of starch, used as an additive, usually at 10, 50 and 90%.[77] These constituents can therefore be subject to microbial degradation, effectively resulting in ''hollowed out'' materials, with concomitantly increased surface area-to-volume ratio, leading to a higher intake of oxygen and water, thus theoretically enhancing hydrolytic and oxidative processes.[51,77] Alas, it has been shown that, at least for some polymers, namely, PE, although the starch component is in fact utilized, the remaining lace-like PE fragments persist,[5,78] resulting in smaller fragments of the polymeric matrix that are no more susceptible to (bio)degradation than the original polymer.[79] Hence, such approaches ultimately lead not to biodegradable polymers, but rather to bio-disintegrated materials, which may actually become more problematic, as the now faster generated smaller particles can have a wider distribution in the environment in which they occur.

Besides polyesters and starch-based polymers, other biopolymers have been the focus of recent attention, such as casein formaldehyde,[80] obtained from milk, wheat or soy bean, among others, or cellulose acetate (CA), obtained by introducing the acetyl radical of acetic acid into cellulose, commonly from cotton or wood.[81] Unlike starch-based polymers and polyesters, however, such materials are not yet presently used in many key applications, such as in the food industry, as more research into their safe use is needed.

Another recent trend in the research into bio-based polymers is the use of non-oil based products and biomass as starting materials. For example, Bio-PE has already been obtained from bioethanol, and the poly(ethylene glycol) component of PET has been obtained from biomass, yielding final products with the same structure as the oil-based plastics and with identical features.[82] Nonetheless, the production costs of these bioplastics remain high, although the prospective perfection of the currently available production technology and development of new synthesis methods will ultimately lead to lower costs and, consequently, to the mass production and use of such materials.

From the previous paragraphs, it becomes clear that the fate of micro- and nanoplastics in the environment remains largely unknown. There is a general consensus that most of these particles end-up in the oceans,[2,7,25,38] and distribution models have been developed[9,83] whose predictions have been supported by some experimental data.[84–86] Degradation of these materials, whether through biotic or abiotic processes or a combination of these, certainly occur, though it should be noted that most laboratorial studies are performed under strictly controlled settings. Thus, failing to fully integrate the real conditions to which plastics are exposed to in nature, such as natural light and temperature cycles or the temporal variations of the materials densities, due to, for example, aggregation and biofilm formation, leading to their distribution across the water column with subsequent varying exposures to temperature, salinity, UV radiation and communities of microorganisms.[2] Laboratorial studies also often resort to homogenous

materials,[61,87,88] thus not reflecting the existence of micro- and nanoplastics with a high diversity of shapes and sizes as they enter the environment, but also in chemical composition, as previously noted. Considering that many of these industrially obtained materials include additives for improving their characteristics, this is something not reflected in the use of pristine materials in these experiments.[25]

Perhaps less important, it should be noted that the ingestion of micro- and nanoplastics and their subsequent excretion may lead to alterations in the materials during the digestive process, potentially resulting in morphological and/or structural modifications of these particles, which, in turn, could affect their fate in the environment. This, however, remains, to this point, merely conjectural and it is likely that such processes could have little impact on the overall fate of micro- and nanoplastics in the environment, whether terrestrial or aquatic.

4 Effects of Nanoplastics

Although generally considered as biochemically inert, plastic products usually contain sub-micron additives, most of which are of small molecular size and that, when subject to degradation processes, whether biotic or abiotic, may leach into the environment, including cells and tissues. Hence, a new class of plastic debris has been increasingly described – plasticides – that may pose significant risks to both the environment and biota. Most of such additives are primarily lipophilic and thus susceptible of penetrating cell membranes, where they can then affect biochemical reactions and induce toxic effects. Although such effects can be inferred to be less prevalent in plant cells, due to the existence of cell walls that may act as a natural barrier against these compounds. Plastics sampled from marine environments have been demonstrated to contain not only deliberately added substances – biocides, flame retardants, surfactants, pigments, lubricants and antistatic agents, among others – but also other contaminants, including organic chemicals, adsorbed from the surrounding medium in which they occur. The plastic production process itself may result in the presence of other compounds, as catalysts of polymerization, initiators and accelerators, referred to as auxiliary substances, that may be emitted during and after production.

Nonetheless, despite the ubiquity of plastic particles in the environment and their closely associated pollutants with potential ecotoxicological effects, the impact of nanoplastics is, for the most part, unknown. Although it may be logical to postulate that both micro- and nanoplastics may yield physical damage, such as perforation of the digestive tract, false sensation of satiety and inanition when ingested, there may be other less obvious effects and some studies have focused on such potential outcomes over numerous organisms and these are summarized in Table 1. Additionally, in Figure 6, a conceptual model illustrates some of the described and theorized potential effects of nanoplastics.

Table 1 The effects (if any) of nanoplastics. The major finding(s) of each study is (are) highlighted. Data partially compiled by da Costa *et al.* (2016).[2] Additional sources[89,90] have been included.

Organism(s)	Contaminant(s)	Particle load exhibiting effects	Major(s) finding(s)
Chlorella sp. and *Scenedesmus* sp.	20 nm PS[a] nanoparticles	>0.55 g L^{-1}	Interference in photosynthesis and promoted ROS[b] production
Scenedesmus obliquus	70 nm PS particles	>30–103 mg L^{-1}	Inhibited growth and reduced chlorophyll cellular concentration
Daphnia magna	70 nm PS particles		Lower reproduction rate and reduced body size
	100 nm fluorescent PS beads[89]	1 mg mL^{-1}	Lower egestion and decreased feeding rates; reproduction not affected
Amphora sp., *Ankistrodesmus angustus* and *Phaeodactylum tricornutum*	23 nm PS particles	10–100 μg L^{-1}	Significant acceleration in EPS[c] assembly
Tigriopus japonicus	500 nm PS particles	1.25 and 25 mg L^{-1}	Decreased fecundity
Mytilus edulis and *Crassostrea virginica*	100 nm PS particles	1.3×10^7 particles L^{-1}	Accumulation of PS particles in the digestive tract
Crassostrea gigas larvae	70–20 μm PS particles	<10^5 particles L^{-1}	No measurable developmental or feeding effects
Mytilus edulis	30 nm PS particles	0.1, 0.2 and 0.3 g L^{-1}	Reduced filtering activity; production of pseudo-faeces
Mytilus galloprovincialis	200 nm PS particles	50 mg L^{-1}	Induction of pre-apoptotic processes
Oryzias latipes	39.4 nm latex particles	10 mg L^{-1}	Particles accumulation in brain, gills, intestine, testis, liver and blood
Oryzias latipes embryos and larvae	50 and 500 nm latex particles	10 mg L^{-1}	Decreased survival rate
Paracentrotus lividus embryos	∼90 nm PS particles	>3.85 mg L^{-1}	Severe developmental defects
Carassius carassius	24 and 27 PS particles	9.3×10^{15} particles L^{-1}	Alterations in the behavior, physiology and metabolism
	28 nm PS particles	10 g L^{-1}	Induced behavioral and fat metabolism changes
Danio rerio[90]	50 nm PS particles	1.5×10^{10} particles mL^{-1}	Larval locomotion and body length reduction
Artemia franciscana larvae	40 nm PS particles	0.5, 25 and 50 mg mL^{-1}	Hampered larvae mobility and induced multiple molting events
Rattus norvegicus	64 nm PS particles	n.d.	Increased neutrophil influx into the lung

[a]Polystyrene.
[b]Reactive oxygen species.
[c]Exopolymeric substances.
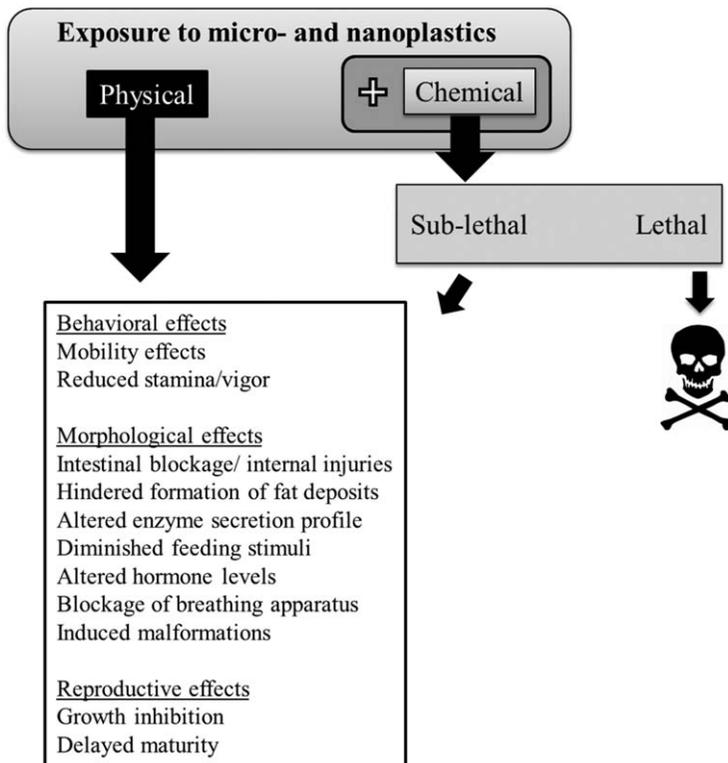
Figure 6 A conceptual model of the described and theorized effects of different sized polymeric materials. Note that exposure to the chemicals alone may yield (some of) the listed effects.
Adapted from ref. 2 with permission from Elsevier, Copyright 2016.

However, in spite of the increasing awareness by scientists, policy-makers and the general public of the potential environmental and health risks these pollutants may pose, and that appear to be substantiated by the afore-mentioned results, the realistic impact that both micro- and nanoplastics remains highly uncertain.

Although ubiquitous, the concentrations at which these materials occur in the environment is still to be accurately determined, and, consequently, most of the studies aiming at assessing potential ecotoxicological effects are frequently based on the use of particle loads that far exceed those commonly found in the environment.[91,92] In fact, as noted by Koelmans and co-workers, natural materials and particles may have adverse effects that are identical or overwhelm those of plastic debris, something often overlooked when evaluating the hazards of such materials.[22]

Nonetheless, some of the bioaccumulative effects of nanoplastics experi-mentally determined should a serve as a cautionary tale. For example, Rossi *et al.* found that PS particles easily permeated into lipid membranes and

that, when dissolved in the membrane, they induced alterations in the membrane structures and severely impacted molecular diffusion, hence influencing cell function.[93] In human lung cancer cells (A549), the uptake of 40–50 nm PS particles has also been demonstrated to be essentially irreversible and that the intracellular concentration of these particles increases linearly.[94] Additionally, slightly larger PS spheres (60 nm) have been reported as exhibiting high toxicity towards macrophage (RAW 264.7) and epithelial (BEAS-2B) cells.[95] As noted in Table 1, Kashiwada[95] reported the accumulation of latex nanoparticles in the gills, intestines, testis, liver and blood of *Oryzias latipes*. However, perhaps of greater concern, this study highlighted the fact that these particles could also be transported to the brain of these organisms, underscoring the potential capability of these materials to cross the blood–brain barrier, a highly selective permeability barrier essential in the protection of the brain from toxins and infections and vital for maintaining the necessary homeostasis required for neuronal function.[96]

The perceived risks that micro- and nanoplastics pose by themselves have been further exacerbated by potential sorption of chemicals by these materials, namely, persistent organic pollutants (POPs),[97] organic compounds highly resistant to environmental degradation through chemical, biological, and photolytic processes. This is of particular relevance for smaller particles, due to their inherent high surface area-to-volume ratio. Consequently, micro- and nanoplastics may become new sources of exposure of chemicals when ingested,[51] as it is possible that these could leach into tissues, leading to long-term toxicity concerns.[2] However, emerging research findings, based on environmentally relevant concentrations of both plastic particles and organic pollutants, have shown that the intake from food and water tends to be the main route of exposure for these pollutants and that those adsorbed in plastic materials constitute a negligible input.[98–101] Hence, the key issues pertaining to the not yet fully understood interaction of micro- and nanoplastics with POPs and their subsequent potential effects on the environment and biota are currently emerging, though it should be noted that the vast majority of known data relates to the aquatic environment.[2] Additional studies, focusing on air and terrestrial media are also necessary, as the same mechanisms could constitute a viable route of exposure of soil (micro)organisms to pollutants, such as pesticides, with ensuing toxicity-related concerns.

In terms of human health, micro- and nanoplastics and their effects are an emerging field. Findings of complementary existing fields of research suggest, however, that there are potential particle, chemical and microbial hazards.[100] When ingested or inhaled, these particles may accumulate and eventually lead to localized particle toxicity by inducing or enhancing immune responses. Therefore, chronic exposure is likely to be of greater concern due to the accumulative effects that may occur. As with other toxic agents, it is reasonable to expect these effects to be dose-dependent, although there is a current lack of robust evidence-base of exposure levels.[22,100]

Despite the limited literature, there is some evidence that points towards the morphological, behavioral and reproductive consequences of exposure to

micro- and nanoplastics. However, these effects have been commonly described based on data obtained using significantly higher concentrations of these materials than those reported in the environment. Hence, more research is needed using environmentally meaningful conditions and focusing on the specific dangers that these particles and/or associated chemicals represent to the environment, biota and, ultimately, to human health.

5   Challenges

In spite of the various studies conducted aiming at determining the potential fates and effects of both micro- and nanoplastics, with an emphasis on the former, there is an increasing consensus on the limited utility of these findings, due to the low degree of similarity between the laboratorial and real-world settings. This is specifically relevant for nanoplastics, as, currently, no specific methods for the sampling and isolation of these materials from environmental samples exist,[2] leaving scientists with no alternative but to exercise some educated guesswork regarding the prevalence of these contaminants in nature. Additionally, due to this lack of environmentally isolated samples, researchers are forced to resort to manufactured nanoplastics, often studying only one type of polymer of a given size and/or shape and color. Although this may contribute to the development of standardized testing procedures and reproducible results, it fails to reflect the wide variety of particles found in the environment.[25] These commercially available polymers, nonetheless, are often sold with a biocide, to prevent bacterial growth, and dispersants, to prevent aggregation, rendering them useless not only in ascertaining the sole effects of the physical characteristics of the studied particles, but also for toxicity tests.[2,17,18]

Technically, as noted, it is necessary to establish widely available routine measurement methods of high accuracy and precision, as well as implement a common, standardized terminology and data reporting, for which a consensus still needs to be reached between all stakeholders.[2,102,103] Only then will it be possible to reach a keen understanding of the behavior of nanoplastics in test systems, although some have suggested that, in the ocean, the characterization of nanoplastics is of low priority. Due to the "retention already occurring in source freshwaters and water treatments plants, due to simple dilution or due to fast aggregation, fouling and/or sinking",[22] which fails to consider the nanoplastics estimated to be directly transferred from the terrestrial and aerial environments to the oceans[2] and the formation of nanoplastics due to fragmentation.

Hence, it becomes necessary to have a more realistic perception of the current prevalence of nanoplastics in the different environmental compartments, and methodologies that pertain the sampling of other nanomaterials in complex matrices may be applicable for the analysis of nanoplastics.[16] For sampling, such methodologies could include ultrafiltration,[104] asymmetric flow-field flow fractionation[105] and hydrodynamic chromatography,[106] among others. Flow-cytometry[107] and multi-angle laser light scattering

(MALLS)[108] have been demonstrated as suitable for the detection nano-sized particles in complex aqueous samples, which may render these techniques susceptible of use for the detection of nanoplastics. For identification, due to the size of the particles (<1000 nm), only a limited number of techniques are capable of achieving sufficient spatial resolution to distinguish individual particles, such as electron microscopy (EM) and atomic force microscopy (AFM), although stimulated Raman spectrometry has shown some potential.[109] Nanoparticle tracking analysis (NTA) has also been suggested as a viable technique for the accurate determination of both concentration and size distributions of nanoplastics in aquatic environments,[110] although NTA showed low accuracy for the size distributions and resulted in the underestimation of small sizes.

For the determination of engineered nanoparticles in tissues (biota), inductively coupled plasma mass spectrometry (ICP-MS) has shown promising results,[111] although the inherent high costs makes this a technique that is not readily available in many laboratories.

Hence, there are numerous analytical methodologies available to examine the presence of nano-sized particles in highly complex matrices. These may be extended towards the analysis of nanoplastics, although there are intrinsic limitations due to the physical and/or chemical principles which they are based on (or the current state of technology). This is best illustrated by element-specific techniques, such as X-ray photoelectron spectroscopy (XPS) or nuclear magnetic resonance (NMR), which may be appealing, as they are also capable of scanning the surface of nanoparticles or their aggregates.[112] Nonetheless, owing to the presence of paramagnetic elements in the matrix, such as Fe^{3+} in a soil sample, the use of such techniques is not possible.[109] The main constraint in the analysis of environmental samples, however, is the expected low levels of nanoparticles in environmental systems,[113] as most specific analytical tools presently have sensitivities that are not appropriate and that require sample preparation, with associated potential artifacts.

6 Conclusions

Nanoplastics are the least known and characterized type of marine litter and, conversely, perhaps the most hazardous one. This may be attributable not only to their inherent physical characteristics, such as the high surface area, which may result in high adsorption rates of organic pollutants with potentially significant bioaccumulation and bioamplification phenomena, but also to their capability in crossing biological barriers, with possible significant ecotoxicological implications.

However, most of these potential effects have been experimentally determined, resorting to conditions of limited ecological and environmental relevance. Nonetheless, a precautionary approach seems warranted, as a reasonable period of time will be necessary to adequately ascertain the concrete ecological effects of these materials in both the environment and biota, if any. Polymer-based products presently constitute a cocktail of

different chemicals and additives, and more data on their fates and effects is necessary, particularly in the marine environment, the *de facto* destination for the millions of tons of plastic litter discarded each year. There are, nonetheless, technical limitations for the accurate determination of their prevalence, and, due to the constraints on the separation, concentration and identification of nanoplastics, the actual occurrence of these materials in the environment remains speculative.

There is a generalized consensus that nanoplastics could constitute a cumulative ecological stress trigger, for example, adding to, as persistent organic pollutants, trace metals and non-polymer-based materials, with potential significant consequences to the environment, and ultimately, to human health. Therefore, the potential hazardous effects of nanoplastics should be considered not in isolation, but rather as an integrative part of marine litter, and, ultimately, in the context of the environment as a whole.

Acknowledgements

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