

MICROPLÁSTICOS E NANOPLÁSTICOS NO AMBIENTE AQUÁTICO: CONTAMINAÇÃO, DETERMINAÇÃO E INTERAÇÃO COM OUTROS CONTAMINANTES

MICROPLASTICS AND NANOPLASTICS IN THE AQUATIC ENVIRONMENT: CONTAMINATION, DETERMINATION AND INTERACTION WITH OTHER CONTAMINANTS

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RESUMO

Introdução: Depois de mais de meio século desde o aumento do despejo de plásticos nos oceanos e outros corpos de água, os danos causados por esses produtos e suas frações foram verificados. Sua presença compromete a qualidade do meio ambiente devido a sua permanência prolongada no habitat e potencial de adsorção de substâncias e liberação de compostos químicos ao meio ambiente responsáveis pela durabilidade do plástico. **Objetivos:** Este artigo visa reunir informações sobre a origem, caracterização e interações de micro e nanoplásticos no meio ambiente e fornecer material atual para os curiosos sobre essa poluição. **Métodos:** Esta revisão foi realizada em busca de artigos sobre micro e nanoplásticos nas bases de dados Science Direct, Springer e Elsevier usando palavras-chave como “microplástico”, “nanoplástico”, “fontes”, “contaminação”, “instrumentos”, “análise”, e “oceano”. Esta revisão utilizou apenas trabalhos publicados e abrange os últimos sete anos de pesquisa sobre o tema a partir da data em que a revisão foi iniciada. O trabalho está estruturado na definição de micro e nanoplásticos, principais fontes, níveis de contaminação, processos de adsorção e técnicas de caracterização. **Resultados:** A degradação desempenha o papel principal na produção de micro e nanoplásticos. Estudos relataram interações entre microplásticos e compostos hidrofóbicos e hidrofílicos e demonstraram que os microplásticos podem concentrar compostos inorgânicos e orgânicos em várias ordens de grandeza, atuando como vetores de copoluentes no meio ambiente. **Discussão:** Fatores como tempo de

exposição, pH, salinidade, temperatura e concentração de adsorbato afetam diretamente os processos de seleção de MP-poluente. O processo de adsorção pode ocorrer na presença de micro e nanoplasticos, uma vez que os poluentes orgânicos têm alta afinidade com materiais sólidos ou particulados. Metodologias e quantificação variam significativamente entre os estudos, dificultando a síntese dos dados. **Conclusões:** Este estudo demonstra que inúmeras técnicas estão sendo modificadas para caracterizar micro e nanopartículas. No entanto, a padronização das metodologias de análise tem se mostrado desafiadora devido à natureza dessas partículas e seu tamanho em escala nanométrica.

Palavras-chave: contaminação ambiental, microplásticos, nanoplasticos, polímeros, espectroscopia, microscópica.

ABSTRACT

Background: After more than half a century since the increase in the dumping of plastics in the oceans and other bodies of water, the damage caused by these products and their fractions has been verified. Its presence compromises the quality of the environment due to its prolonged permanence in the habitat and potential for the adsorption of substances and release of chemical compounds to the environment responsible for the durability of the plastic. **Aims:** This paper aims to gather information about the source, characterization, and interactions of micro- and nanoplastic in the environment and provide current material for those curious about this pollution. **Methods:** This review was conducted searching for papers on micro and nanoplastics on Science Direct, Springer, and Elsevier databases using keywords such as “microplastic”, “nanoplastic”, “sources”, “contamination”, “instruments”, “analysis,” and “ocean”. This review used only published works and comprise the last seven years of research on the topic from the date the review was initiated. The work is structured in the definition of micro and nanoplastics, main sources, levels of contamination, adsorption processes, and characterization techniques. **Results:** Degradation drives the main role in producing micro- and nanoplastic. Studies have reported interactions between microplastic and hydrophobic and hydrophilic compounds and demonstrated that microplastics can concentrate inorganic and organic compounds in several orders of magnitude, acting as vectors for co-pollutants in the environment. **Discussion:** Factors such as exposure time, pH, salinity, temperature, and adsorbate concentration directly affect MP-pollutant selection processes. The adsorption process might happen in presence of micro- and nanoplastic since organic pollutants have a high affinity with solid or particulate materials. Methodologies and quantification vary significantly among studies making it difficult to synthesize data. **Conclusions:** This study demonstrates that numerous techniques are being modified to characterize micro- and nanoparticles. However, standardizing analysis methodologies has proven challenging due to the nature of these particles and their nanometer-scale size.

Keywords: environmental pollution, microplastic, nanoplastic, polymer, spectroscopy, microscopy.

1. INTRODUCTION

Micro and nanoplastic pollution arise mainly due to improper disposal of macroplastics (Thompson *et al.*, 2004) from continental sources, for example, dumping of domestic waste, tourism, and fishing activities, and marine sources such as litter from oil platforms and commercial and military and research vessels (Sheavlyand Register, 2007). After more than half a century since the increase in the dumping of plastics in the oceans and other bodies of water (GESAMP, 2015; Thompson *et al.*, 2004), the harm caused by these products and their fractions in the ocean has been verified (Courtene-Jones *et al.*, 2019; Setäläet *al.*, 2018; Sheavly& Register, 2007). From the 1970s, scientific literature began to present studies that accused the presence of

microplastics in the marine environment (Carpenter *et al.*, 1972; Carpenter and Smith, 1972), which raised the question of how these particles interact with the environment and with organisms (GESAMP, 2015).

This statement can be observed due to the entry of microplastics into the food web of the marine ecosystem, present in the cycle from the food base, in phytoplankton and filtering organisms, to mammals and seabirds through ingestion, inhalation, or adhesion of these components (Arthur *et al.*, 2008; Courtene-Jones *et al.*, 2019; Ivar Do Sul and Costa, 2014; Setäläet *al.*, 2018; Yong *et al.*, 2020; Yuan *et al.*, 2022). Additionally, its presence compromises the quality of the environment due to its prolonged permanence in the habitat and potential for the

adsorption of substances present in the environment and release of chemical compounds responsible for the durability of the plastic (Thompson *et al.*, 2004; Yong *et al.*, 2020). Another problem is the origin of the microplastic since, once released into the environment, the action of winds and currents is capable of transporting it over long distances, hampering the identification of the source and, consequently, the possibility of remedying the origin of the problem (Hidalgo-Ruzet *et al.*, 2012; Yong *et al.*, 2020).

In addition to the biota, microplastic distribution in the marine environment occurs on the surface, water column, deep waters, and sediment (Courtene-Jones *et al.*, 2017; Garcia *et al.*, 2020; G. Peng *et al.*, 2020; Peng *et al.*, 2018). Therefore, they are usually classified as beached marine debris (BMD, marine debris depositing on the beach), floating marine debris (FMD, marine litter floating on the sea surface), and submerged marine debris (SMD, marine debris submerging in the sea water), and this will command what sampling type (Hinojosa & Thiel, 2009). The density of plastic, when lower than that of saline water, allows it to remain in the liquid fraction, while the action of photodegradation on plastic fragmentation, its composition, and biofouling end up ensuring its presence in the deepest regions of the oceans and sediment (G. Peng *et al.*, 2020), with the ocean floor having the highest concentrations of microplastic (Kane *et al.*, 2020). Both horizontal ocean circulation and surface currents, bottom topography, and seasonality can significantly influence the number of microplastics (Kane *et al.*, 2020).

This paper aims to gather information about the source, characterization, effects of micro- and nanoplastic in the environment, sampling techniques, and laboratory analysis from the available literature. This is important to connect relevant information about this area of research and thus facilitate access to what you need to know about the subject. Thus, it is expected to contribute to science in this area of study by providing current and primordial material for those curious about micro- and nanoplastics and identifying possible gaps in the knowledge.

2. METHODS

This most of the review was conducted in 2022 by searching for papers on micro and nanoplastics on database sites such as Science

Direct, Springer, and Elsevier. Some of the keywords used for research on these platforms were “microplastic”, “nanoplastic”, “sources”, “contamination”, “instruments”, “analysis,” and “ocean”. This review used only published works, discarding monographs, notes, theses, dissertations, and presentations of works in congresses. Most articles used comprise the last seven years of research on the topic from the date the review was initiated. The work is structured in the definition of micro and nanoplastics, their main sources, levels of contamination, adsorption in microplastics, how the properties of sea water affect the adsorption in micro and nanoplastics, and analysis techniques for micro and nanoplastics.

3. RESULTS AND DISCUSSION

3.1 Definitions of micro and nanoplastic

Plastics are polymers created commercially with different chemical compositions and added additives to improve their physical and mechanical properties (Gigault *et al.*, 2018). As a result, plastic fragments can break down into smaller pieces and degrade further when exposed to UVB radiation in sunlight (Moore, 2008) and other environmental factors. A particular concern is the smaller pieces of plastic debris, including those not visible to the naked eye, referred to as “microplastics” (Andrady, 2011; Van Cauwenberghe *et al.*, 2015).

Microplastics are mainly composed of polyvinyl chloride (PVC), nylon, polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS), as well as other polymers such as polyvinyl alcohol (PA), and polyamide (PA) (Andrady, 2017). As proposed by the European (Marine Strategy Framework Directive-MSFD, 2008/56/EC), microplastic nomenclature (nano-, micro-, meso- and macroplastic) is based on size, and thus is composed of particles: smaller than 1 μm (nanoplastic); 1 μm to 5 mm (small- and large- microplastic) and larger than 5 mm (meso- and macroplastic) according to Figure 1 (Galganiet *et al.*, 2013; Van Cauwenberghe *et al.*, 2015).

The importance of having a definition regarding the size of plastic fragments that are invisible to the naked eye lies in understanding their degree of damage and in which oceanic compartment they are most likely to be found (Cole

et al., 2011; GESAMP, 2015, 2016; Caruso, 2019). While nanoplastic generally, it has been assumed that they fall within the range of other types of nanoparticles, there is still no established definition (Ferreira *et al.*, 2019; Gigault *et al.*, 2018). However, nanoplastic as particles with sizes of < 1 μm and that exhibit a colloidal behavior is the most accepted definition until now, although other authors also suggest sizes of < 100 nm (Gaylarde *et al.*, 2021; Gigault *et al.*, 2018).

3.2 Sources of micro- and nanoplastics

As a result, we have analyzed 138 papers, and many of them have found that micro and nanoplastics from polymers are produced intentionally for specific purposes. Thereby demonstrating anthropogenic activities as the main sources of this pollution. According to Rios Mendoza, Karapanagioti, and Álvarez (2018), the main sources of micro- and nanoplastics in the marine environment are from polymer nanoparticles that are produced intentionally for specific purposes (e.g., cosmetic and personal care products, ink for 3D printers, and others), others include synthetic clothing, abrasives found in cleaning products, drilling fluids, and air-blasting media, so-called primary microplastics. On the other hand, secondary microplastics are from chemical, physical and biological processes in the environment. Since the patenting of microplastic scrubbers within products in the 1970s, plastics have been used in cosmetics, personal care, and others (Fendall & Sewell, 2009).

Typically denominated as “micro-beads” or “micro-exfoliates”, the plastics vary in composition, size, and shape depending upon the product (Auta *et al.*, 2017). Gregory (1996) reported the presence of polyethylene and polypropylene granules (< 5 mm) and polystyrene spheres (< 2 mm) in a cosmetic product. Chang (2013) estimated that approximately 5000 g of microplastics go into the waste stream on a yearly basis due to the usage of approximately 5000 g of polyethylene beads in facial cleansers. Effluents from Wastewater Treatment Plants also emerge as one way of releasing microplastic, especially synthetic fibers from clothing and using personal care products (Gouin *et al.*, 2011; Murphy *et al.*, 2016).

One estimation is that the US population emits about 263 tons yr^{-1} polyethylene microplastics (Gouin *et al.*, 2011). According to

Murphy *et al.* (2016), Wastewater treatment works located on the river Clyde (Glasgow) release about 65 million microplastic particles into the receiving water daily. Since the patenting of microplastic scrubbers within products in the 1970s, plastics have been used in cosmetics, personal care, and others (Fendall & Sewell, 2009). Typically denominated as “micro-beads” or “micro-exfoliates”, the plastics vary in composition, size, and shape depending upon the product (Auta *et al.*, 2017).

The distinction between the primary and secondary sources of micro- and nanoplastic is based on whether the small plastics were originally manufactured to be that size (primary) or whether they have resulted from the breakdown of larger plastic items such as plastic bags and fishing nets (secondary). A combination of the properties of the polymer (e.g., size and density), as well as sunlight and temperature, influence the disintegration of macroplastic debris (Auta *et al.*, 2017). The ultra violet radiation in the sun causes oxidation of the polymer matrix, which leads to the cleavage of bonds, and this process is most effective on beaches due to high UV light, physical abrasion (waves, oxygen availability), and turbulence (Andrady, 2011; Auta *et al.*, 2017; Cole *et al.*, 2011; GESAMP, 2015; Wagner *et al.*, 2014). After this “start” fragmentation, the physical processes continue, and chemical and biological processes are added to both the superficial and deep ocean, in one-way unknown yet (Cole *et al.*, 2011).

Microplastics can enter the marine environment via estuarine systems, beach coastlines, directly at sea from harbors, vessels, and platforms, or by wind-induced transport in the atmosphere (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection GESAMP, 2016). Fragmentation and degradation of macroplastics drive the main role in producing smaller plastics, but the detailed processes are poorly known. Methodologies to define microplastics and nano-sized plastic debris, sampling procedures, and quantification vary significantly among published studies, source sectors, and regions of the planet, making it difficult to synthesize data across research programs. Different sources, fates, and impacts of microplastic pollution were summarized by (Nolasco *et al.*, 2022) in a DPSIR framework, as shown in Figure 2.

3.3 Microplastics contamination levels

Microplastics (MPs) are considered sedimentary components in marine and terrestrial

environments (Rillig, 2012; Thompson *et al.*, 2009). Properties to their physical-chemical properties, such as superior hydrophobicity and surface areas, presented great adsorption of persistent organic pollutants and toxic metals (Rochman *et al.*, 2013). In the case of secondary microplastics, which are characterized by undergoing successive fragmentation processes in the environment resulting from weathering processes, with the help of physical-chemical agents, mechanical stresses, and heating (Schmid *et al.*, 2021), these microparticles have changes in the composition of their surface, increasing the amount of oxygenated functional groups and, consequently, greater interaction with hydrophilic organic matter (Hüffer *et al.*, 2018).

MPs may contain, in addition to additives such as pigments and stabilizers from the industrial process (Fahrenfeld *et al.*, 2019), pharmaceuticals (F. fei Liu *et al.*, 2019), pesticides, herbicides (Rodrigues *et al.*, 2019), polycyclic aromatic hydrocarbons (PAHs) (Avio *et al.*, 2017); polychlorinated biphenyls (PCBs) and nonyl-phenols (Mato *et al.*, 2001; W. Wang & Wang, 2018), toxic metals (H. Chen *et al.*, 2015; Gao *et al.*, 2019; Turner & Holmes, 2015) and additives such as plasticizers, flame retardants, and microbial agents (Gao *et al.*, 2019; Law & Thompson, 2014) that are found in the marine environment. This characteristic of MP makes them the potential of different pollutants for the marine environment. Once present in the marine ecosystem, these classes of compounds have represented a risk for the reproduction and growth of species in these environments (Besseling *et al.*, 2014; Della Torre *et al.*, 2014; Velzeboer *et al.*, 2014). Factors such as exposure time, pH, salinity, temperature, and adsorbate concentration directly affect MP-pollutant selection processes.

Hildebrandt *et al.* (2021) in their study evaluated the sorption of metals and metalloids in MP and observed that reduced sizes (63-125 μm) of MP present a greater tendency to present the trojan horse effect for dissolved metallic cations: Potential insertion of metals and metalloids of recognized toxicity, along the trophic levels of the food chain. The vast majority of studies involving organic contaminants in the literature report interactions between MP and hydrophobic compounds. However, some works have reported interactions between secondary MP and hydrophilic compounds. Gao *et al.* (2019) compare the levels of metals and 16 USEPA-priority PAHs adsorbed by MPs (polypropylene).

Results monitored in Maida and Huangdao in China indicate that 13 of the 16 PAHs

were found ranging from 0.072 to 0.261 $\mu\text{g/g}$ (mean: 1.167 $\mu\text{g/g}$) and 0.114 to 0.245 $\mu\text{g/g}$ (mean: 0.180 $\mu\text{g/g}$), respectively, suggesting low and moderate levels of local data (Baumard *et al.*, 1998). In addition, the concentration of toxic metals observed in the polypropylene samples varied in the same magnitude as the PAHs: Mn (0.352 and 0.787 $\mu\text{g/g}$), Pb (0.018 and 0.015 $\mu\text{g/g}$), Cu (0.018 and 0.018 $\mu\text{g/g}$), and Cr (0.007 and 0.010 $\mu\text{g/g}$). Wardrop *et al.* (2016) verified the presence of polybrominated diphenyl ethers (PBDEs) adsorbed on microplastics (microspheres) from personal hygiene products present in fish tissues. The highest levels of PBDEs detected in the fish tissue samples were observed after 21 days of exposure, showing a tendency to accumulate during the experiment to 9.72 ng g^{-1} at 63 days.

3.4 Principles of microplastics adsorption at solid surfaces

A number of studies have also demonstrated that microplastics adsorb both inorganic and organic compounds and can concentrate them several orders of magnitude than the levels found in their surrounding environment, acting as vectors for co-pollutants in the environment (Rodrigues *et al.*, 2019). According to Rist and Hartmann (2018), the adsorption process is more pronounced for inorganic engineered nanomaterials – or inorganic carbon in the case of C_{60} fullerenes and CNTs, and the absorption process is more pronounced for polymer particles. In the case of polymer particles, the sorption may also be a combination of ab- and adsorption processes, as shown in Figure 3. Although there are a larger number of contaminants classes, most studies are restricted to the following adsorbates; persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDTs), and toxic metal ions (Alimi *et al.*, 2018; G. Liu *et al.*, 2019; Rodrigues *et al.*, 2019; F. Wang *et al.*, 2015).

To deeply understand the dynamics of microplastic in marine environments, it is important to study its propriety as a potential adsorbent or absorbent. Sorption of a compound can refer to two different processes: absorption and adsorption. The first one is the process by which atoms, molecules, or ions enter a bulk phase of a liquid, gas, or solid. The second one is the adhesion of atoms, ions, or molecules from a fluid (gas, liquid, or dissolved solid) to a solid surface, making it possible to separate the components from the fluid.

Sorption can occur through absorption processes due to hydrophobic interactions of the aliphatic and aromatic groups of a contaminant with the lipid fraction of suspended solids and/or bacterial cells. In addition, sorption can occur through adsorption processes due to the electrostatic interaction between the negative surface of microorganisms and positively charged groups of a compound (Bernal *et al.*, 2018). The absorption mechanism is related to the compound hydrophobicity, the partition coefficient octanol-water (K_{ow}), and is expressed as $\text{Log}K_{ow}$ for neutral compounds. Contaminants with $\text{Log}K_{ow} \geq 2$ as lipophilic, and those with $\text{log } K_{ow} \leq 2$ as hydrophilic.

Volatilization occurs for compounds with high Henry constants (Bernal *et al.*, 2018). This parameter allows predicting the potentiality of the substances to be incorporated into the biomass by their easiness to be adsorbed or not to organic matter, among other phenomena. The adsorption mechanisms are related to the partition coefficient K_d . Compounds with $\text{Log}K_d > 2.7$ have high adsorption potential, whereas compounds with $\text{Log}K_d < 2.7$ possess low adsorption potential.

The adsorption process might happen with organic and inorganic compounds when in the presence of microplastics since, especially, organic pollutants have a high affinity with solid or particulate materials, especially in the aquatic environment due to their hydrophobicity, tending to adsorb and accumulate on the surface of the plastic (Teuten *et al.*, 2009). Most of these pollutants are bio-accumulative, and some are toxic or deleterious. If leached by microplastics and assimilated by an organism, they can be introduced into the food chain (Figure 4) (Browne *et al.*, 2008; Munoz-Pineiro, 2018). Therefore, adsorbents are generally solid with porous particles. Once the adsorbed components are concentrated on the outer surface, the larger this outer surface per unit of solid mass, the more favorable the adsorption process.

The species that accumulates at the material interface is usually called *adsorbate*, and the solid surface on which the adsorbate accumulates is called *adsorbent* (F. F. De Oliveira *et al.*, 2020). The adsorption separation processes are based on three distinct mechanisms: the steric (1), equilibrium (2), and kinetic (3) mechanisms. For the steric mechanism, the pores of the adsorbent material have specific dimensions, which allow certain molecules to enter, excluding others. For the equilibrium mechanisms, the different solids can accommodate different species of adsorbates, which are preferentially

adsorbed to other compounds.

The kinetic mechanism is based on the different diffusivities of the different species in the adsorbent pores (Kärger *et al.*, 2012). Depending on the nature of the forces involved, adsorption can be classified as to its intensity into two types: physical and chemical adsorption. In the case of physical adsorption (Physisorption), the force that attracts the adsorbate to the surface of the adsorbent involves a relatively weak interaction that can be attributed to the van-der Waals forces, which are similar to the forces of molecular cohesion (Melo *et al.*, 2016; Vidal *et al.*, 2012). In contrast, chemisorption involves the exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction.

The concepts of chemisorption and physisorption are different; however, the two adsorption mechanisms are not completely independent. The distinction as to whether the species is physically or chemically adsorbed is not very clear, as both processes can often be described in terms of the principles of physical adsorption (Quadros Melo *et al.*, 2016). Since it involves the breaking and formation of new chemical bonds and, therefore, greater energies than physisorption.

The differences between physical and chemical adsorption can be summarized as follows: Chemical adsorption is highly specific, and not all solid surfaces have active sites capable of chemically adsorbing the adsorbate. Not all molecules present in the fluid can be chemically adsorbed, only those capable of binding to the active site. Physical adsorption, unlike chemical adsorption, is nonspecific; that is, it occurs on the entire adsorbent surface. From the thermodynamic point of view, the heat involved in the physisorption is generally below 10 kcal mol^{-1} .

That is, in the order of condensation/vaporization process. In the case of chemical adsorption, the heat of adsorption is of the order of reaction heat, therefore, above 20 kcal mol^{-1} . Another way of understanding physical adsorption suggests that it occurs when intermolecular forces of attraction between molecules in the fluid phase and the solid surface of the adsorbent are greater than the attractive forces between molecules in the fluid itself. This type of adsorption is fast and reversible due to the action of weak intermolecular attraction forces between the adsorbent and the adsorbed molecules. It should be added that since there is

no formation or breaking of bonds, the chemical nature of the adsorbate is not altered. Another peculiarity of physical adsorption is the possibility of having several layers of adsorbed molecules.

The adsorption phenomena result from a combination of the types of forces involved in physical and chemical adsorption. Thus, several factors influence the adsorption process depending on the adsorbent and adsorbate characteristics. Among the characteristics of the adsorbent that affect adsorption, surface area, pore size, density, functional groups present on the surface, and hydrophobicity of the material can be mentioned. For polymers, it can also be included: type of polymer, color, size, and degree of weathering, as well as the environmental factors, such as pH, salinity, and water temperature (Quadros Melo *et al.*, 2016; Ziccardi *et al.*, 2016). On the other hand, the nature of the adsorbed depends on the polarity, size of the molecule, solubility, and acidity or basicity of contaminants (adsorbates).

3.5. Mechanisms of adsorption in micro- and nanoplastics in ocean environments: effect of pH, temperature, salinity, and others

Complete polymer degradation is complex and highly slow (Frias *et al.*, 2010; Rios Mendoza *et al.*, 2018). The abiotic degradation process cause failures in the structures of microplastics, which may increase the contact surface for organic contaminants and microbial cells. Among the polymers with lower crystallinity, polyethylene, polypropylene, and nylon can be mentioned, and in contrast, polystyrene has a higher crystallinity (Syberg *et al.*, 2015). Considering the variation of the aquatic environment conditions, as ocean and microplastics physicochemical properties, Rochman *et al.* (2013) studied the sorption of organic contaminants to five types of plastic pellets and their implications for plastic marine debris.

According to the authors, High-density polyethylene (HDPE), Low-density polyethylene (LDPE), and polypropylene adsorbed higher concentrations over time of PAHs and Polychlorinated Biphenyls (PCBs) when compared to PET and PVC, showing that rubbery polymers have a greater ability to attract and carry Persistent organic pollutants (POPs) on their surface than vitreous ones. Besides that, PE has a higher superficial area and porous volume than other polymers. The adsorption capacity of MPs can be affected by several factors. The variation of pH, temperature, salinity, and presence of organic

matter can cause changes in the interaction of the polymer with the organic contaminants of the environment.

The increase in the salinity of the medium can decrease the adsorption capacity of hydrophobic compounds in the sediments and increase nano and microplastics (Velzeboer *et al.*, 2014). According to Bakir, Rowland, and Thompson (2014), when the pH decreases and the temperature increases, the desorption phenomenon can occur. Depending on the continuity of these physical property changes, this phenomenon can occur with greater or lesser frequency. G. Liu *et al.* (2019) studied the influence of salinity and pH in the MPs adsorption process, and they showed that changes in the pH of the medium did not significantly vary the adsorption. The capacity adsorption followed: PS > PE > PVC. However, with the increase in salinity, a greater MPs adsorption capacity was found due to the salting out effect.

The increase in salinity can also cause the polymers to agglomerate, causing the reduction of active sites for adsorption (Xie *et al.*, 1997). The effect of salinity may not have influenced adsorption behavior, as seen by Guo, Chen, and Wang (2019). In the MPs used, the adsorptive capacity was not significantly altered with the introduction of NaCl into the medium. It can be observed that this condition does not interfere with the transport of organic contaminants. The presence of salts in an aqueous solution can modify the solubility and properties of existing organic compounds and MPs solubility. According to G. Liu *et al.* (2019), in ionic strength experiments, the PVC went to the bottom in NaCl presence, and the PE and PS stabilized on the surface.

Studies have shown that plastics with lighter shades of color have a lower rate of adsorption of low molecular weight PAHs, whereas darker-colored plastics adsorb higher molecular weight PAH (Fisner *et al.*, 2017). Frias *et al.* (2010) studied two Portuguese beaches, identified mainly PP, PE, and PS, and found high levels of PAHs, PCBs, and DDTs in all the collected pellets, with higher levels in black and aged pellets. Besides, found a higher concentration of POP adsorbed in dark pellets, PAHs adsorbed in aged black pellets, and PCB in black pellets, while DDTs were found in aged plastics. According to Frias *et al.* (2010), PE is the most produced plastic and shows higher sorption capacity than other plastics for most contaminants, while PVC generally accumulates lower amounts of contaminants (Alimi *et al.*, 2018).

Differently, G. Liu *et al.* (2019) reported that the sorption of the phthalate compounds on the three microplastics followed the order of PS > PE > PVC, indicating that the chemical properties of microplastics played an important role in their sorption behaviors. Additionally, environmental conditions simulations showed that pH and natural organic matter had no significant impact on sorption by microplastics. At the same time, the presence of NaCl and CaCl₂ enhanced the sorption because of the salting-out effect. However, toxic metals such as aluminum, copper, silver, zinc, lead, iron, and manganese have rarely been detected on plastic pellets sampled in seawater (Ashton *et al.*, 2010). Since the surface area plays an important role in the adsorbent material, it is important to understand the weathering of plastics in ocean environments and how this might alter the rugosity and surface area of the plastic.

The degradation process does not break down the macroplastics entirely, but they reduce their size, resulting in plastic fragments on the micro and nano scale. Hence, it is known that the smaller the size of the plastics is, the greater their adsorption capacity due to their surface area and the existence of active sites (Rodrigues *et al.*, 2019). The fragmentation process might change the polymer's chemical structure, oxidizing them and creating new functional groups (Costa *et al.*, 2016).

Polymers have crystalline and amorphous regions in their structure, which influence their capacity and mechanisms of adsorption. The organic compounds have more affinity to the amorphous regions of the polymer materials. Therefore, the lower the structural crystallinity of the plastic, the greater the adhesion of organic compounds. The relationship between adsorption and salinity reducing the adsorptive capacity in the medium can be explained by two reasons: (1) the increase in ionic strength in the medium will affect the aggregation of the adsorbent nanoparticles (2) sodium chloride (NaCl) and calcium chloride (CaCl₂) ions would be penetrated in the double layers of the nanoparticles of the adsorbents, thus increasing their density, decreasing their repulsion, thus compacting the structures and disfavoring the adsorption (Zhang *et al.*, 2010).

3.6. Analytical techniques and methods used for characterization and quantification of micro- and nanoplastics

3.6.1. Sampling

The samples can be environmental waters, sediments, biota, food, and even sewage and drinking water, so the particles present together with the microplastics are diverse and complex (Schwaferts *et al.*, 2019). Silva *et al.* (2018) have mentioned that neuston, trawl, and catamaran networks are used in surface waters, and bongo nets are more frequent in mid-level waters (Figure 5). To analyze microplastics in marine environments, the National Oceanic and Atmospheric Administration of the United States (NOAA) proposes laboratory procedures with specific recommendations for preparing and digestion water and sediment samples for subsequent identification and quantification (Masura *et al.*, 2015).

Several methods are used for this purpose (Ivleva *et al.*, 2017; Schwaferts *et al.*, 2019). According to Masura *et al.* (2015), the samples are treated with hydrogen peroxide (H₂O₂) in the presence of iron II to digest organic matter. Then, a separation of the plastic particles by density difference occurs by adding a solution of sodium chloride (NaCl), sodium iodide (NaI), or zinc chloride (ZnCl₂). Although sodium chloride is cheaper, it has a lower density (1.2 g/cm³), so certain denser plastic particles may not be separated successfully.

The possible methods used to analyze micro/nanoplastic in different types of samples are summarized in Figure 6. While sodium iodide (1.6 - 1.8 g / cm³) and zinc chloride (1.5 - 1.7 g / cm³) could obtain better results (Masura *et al.*, 2015), other treatments used for digestion of the matrix, including acid treatment with nitric acid (Lu *et al.*, 2016; Rist *et al.*, 2017), alkaline treatment with sodium hydroxide (Q. Chen *et al.*, 2017; Rist *et al.*, 2017), enzymes such as proteinase K (Correia & Loeschner, 2018; Rist *et al.*, 2017) and a combination of potassium hydroxide with 5% hydrogen peroxide and 2.7% of methanol for biological materials digestion (Fraissinet *et al.*, 2021). In addition, other procedures can be used to pre-concentrate and separate the samples because the mass of microplastic/nanoplastic particles can be very low. These procedures are membrane filtration, ultrafiltration, dialysis, ultracentrifugation, and evaporation of solvents for preconcentration and hydrodynamic chromatography, by size exclusion chromatography and high-performance chromatography, also capillary electrophoresis, among others (Schwaferts *et al.*, 2019).

The analytical procedure for sampling and sample preparation depends on the matrix to be analyzed since plastic contamination is found in

the main terrestrial and marine environments. Due to the different matrix and particle morphologies, each sample may require specific treatments and equipment configurations. Therefore, it is essential to select the treatment and pre-treatment method that is most convenient and according to the type of sample. Additionally, for the chemical characterization of micro- and nanoplastic particles, it is necessary to remove natural organic matter, organisms, and tissues from the particles to avoid interferences.

3.6.2. Morphological characterization of micro- and nanoplastic particles

For the morphological characterization of the micro- and nanoplastics particles, different techniques have been used and can be separated into the following: light scattering techniques and microscopic techniques, as shown in Figure 6. Choosing the appropriate technique for morphological characterization depends on the specific objectives of the research and the desired information to be obtained from the particles.

3.6.2.1 Light scattering techniques

Light scattering techniques have been used in different studies to characterize the morphologies of micro- and nanoplastic such as Dynamic light scattering (DLS), Electrophoretic light scattering (ELS), and Multiangle light scattering (MALS). The DLS technique is widely used to characterize particle size and especially nanoplastic particles, primarily due to its easy application, low cost, direct coupling, and no invasiveness (Schwaferts *et al.*, 2019). However, this method is very sensitive to contaminants such as matrix residues, aggregates, or dust that can mask the analyte (Laborda *et al.*, 2016). It is important to mention that DLS may overestimate large particles because it uses theoretical models based on spheres and performs best with monodisperse suspensions.

Furthermore, it does not distinguish different composition particles with similar structures since it does not provide chemical information (Schwaferts *et al.*, 2019). The principle of ELS is similar to DLS. The ELS method provides an electrophoretic velocity produced by the fluctuation of laser intensity in a well-defined electric field caused by particle movement (Xu, 2015). The plastic particles in environmental samples are exposed to weather, and that causes changes in their surface charge due to oxidation (Lambert and Wagner 2016b).

Hence, detecting surface alterations of

particles can indicate their environmental residence time. In this technique, the electrophoretic velocity is correlated with the shear surface charge of the particle, known as zeta potential, thus, providing valuable information about the aging of plastic particles (Schwaferts *et al.*, 2019). MALS obtains information on particle size by recording the laser light that is scattered at different angles (Schwaferts *et al.*, 2019). Polydisperse samples can be coupled to AF4 to obtain relevant information on micro and nanoplastic particles (Correia & Loeschner, 2018; Mintenig *et al.*, 2018) (Figure 7).

When combined with Size Exclusion Chromatography (SEC), MALS can accurately measure polymer mass and size distributions (Wyatt, 1998). SEC-MALS is useful for characterizing branched polymers since it provides information on the chain structure from the molar-mass size ratio (Podzimek *et al.*, 2001). Combining MALS with Field Flow Fractionation (FFF) yields better resolution than TEM measurements, enabling more precise determination of particle size distributions (Wyatt, 1998).

Other methods based on light scattering (LS) are laser diffraction (LD) and Nanoparticle Tracking Analysis (NTA). Thereby, LD allows the size of solid particles in liquid media in a wide range of 10 nm to 10 mm (Xu, 2015). On the other hand, NTA can be an alternative to DLS to determine the particle size distribution in polydisperse samples since it suffers less perturbation from large particles (Filipe *et al.*, 2010)

3.6.2.2 Microscopic techniques

3.6.2.2.1 Electron microscopy (EM)

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are considered adequate techniques for the morphological characterization (size, shape, texture) of micro and nanoplastics in simple matrices and from fragmentation studies (Correia & Loeschner, 2018; Lambert & Wagner, 2016a; Pico *et al.*, 2019). TEM uses high-voltage electron acceleration and thin samples to detect electron beams, enabling the imaging of very small particles (Schwaferts *et al.*, 2019). SEM imaging gives morphological information about the particles by detecting lower energy secondary electrons caused by the electron beam (Schwaferts *et al.*, 2019). TEM provides information about the interior of the particles, contrary to SEM, which allows knowing surface

details. If SEM and TEM are coupled with Energy Dispersive Spectroscopy (EDS) (e.g., Energy-dispersive X-ray (EDX), as shown in Figure 8) or Electronic Energy Loss Spectroscopy (EELS), information on the elemental composition can be obtained (Laborda *et al.*, 2016).

As reported by Oriekhova & Stoll (2018), SEM allows analyzing the behavior of hetero-aggregation of nanoplastics in the presence of organic and inorganic matter due to its topological surface strength. However, Magri *et al.* (2018) point out that a disadvantage of general electron microscopy (EM) is the representativeness because the number of analyzed particles can be too low, and the image section cannot represent the entire sample homogeneously. Other EM-based techniques that have been employed include Environmental Scanning Electron Microscopy (ESEM), used to analyze humid environmental samples in a low-pressure atmosphere controlled by nitrogen to avoid degradation (Schwaferts *et al.*, 2019). Moreover, Cryogenic Electron Microscopy (Cryo-EM), a method reported by Cai *et al.* (2018), is based on freezing a dispersion of the sample with nitrogen or liquid ethane, nitrifying the water instead of crystallizing it, thus preserving the integrity of the sample. Schwaferts *et al.* (2019) recommend sublimating ice droplets or identifying them using EDS, as ice droplets may be present and mistaken for plastic particles.

3.6.2.2.2 Optical microscopy

Fluorescence microscopy is a common technique for analyzing micro and nano plastics in organism samples with fluorescently marked particles, using a confocal pinhole to block the light of the lateral parts allowing a resolution close to the diffraction limit (A. Dawson *et al.*, 2018; A. L. Dawson *et al.*, 2018). This technique can locate smaller particles as long as they emit sufficient fluorescence signals (Schwaferts *et al.*, 2019). Sancataldo *et al.* (2020) characterized four different types of microplastic such as LDPE, PS, PET, and Nylon, stained with Nile Red in water samples using a confocal fluorescence microscopy image as shown in Figure 9.

Moreover, Nolasco *et al.* (2022) used stereoscopic microscopy to morphologically analyze microplastics in water samples, classifying them into fibers, fragments, sheets, and foam based on their shapes (Figure 10). The stereo microscope produces high-quality images that provide a full three-dimensional effect by observing the specimen from slightly different

angles with both eyes. The microscope typically has a large depth of field and a long working distance, making it easy to manipulate and interact with the specimen (Hammond & Evennett, 2005). However, stereo microscopy is a preliminary test used to visually inspect the sample for its general appearance, such as its shape, color, texture, and other features (Buzzini & Stoecklein, 2005), to determine whether or not it may be a plastic material.

3.6.2.2.3 Scanning probe microscopy

Nolte *et al.* (2016) investigated the influence of particle surface functionality and water hardness on nano-plastic adsorption to algae cell walls using Atomic Force Microscopy (AFM). The study revealed that neutral and positively charged plastic nanoparticles were adsorbed more strongly onto the algae cell wall than negatively charged plastic particles and suggested that Dynamic Force Microscopy is a useful ecotoxicity screening tool for studying bio-adsorption without the influence of agglomeration. Additionally, Nolte *et al.* (2016) reported that this technique allows liquid sample analysis and can be used in combination with infrared (A. Dazzi *et al.*, 2015) or Raman spectroscopy (Kumar *et al.*, 2015) to provide chemical images of the samples.

AFM provides height information of the sample by recording the deflection of a cantilever caused by electrostatic or van der Waals interactions (Tiede *et al.*, 2008). Techniques based on Scanning Probe Microscopy (SPM) utilize a sensor for scanning and interacting with the surface of a sample. It is not limited by the diffraction of incident light (Lin *et al.*, 2014). In Scanning Tunnel Microscopy (STM), a topographic image is provided by scanning the surface of the sample using a tunneling current (Schwaferts *et al.*, 2019). Confocal Laser Scanning Microscope (CLSM), a variant of SPM, is ideal for detecting and characterizing nanoplastics in matrices such as freshwater fish and crustaceans (Pico *et al.*, 2019).

Another technique is Near-field Scanning Optical Microscopy (NSOM). This confocal optical microscope detects fluorescence by scanning the sample with an approximate resolution of 200 nm at the diffraction limit (Chae *et al.*, 2018; A. L. Dawson *et al.*, 2018). The NSOM tip has a small aperture where the laser light is conducted, and the light becomes highly localized due to the aperture being smaller than the laser wavelength (Heinzelmann & Pohl, 1994). CLSM and NSOM provide high-resolution micro and nano-plastic

imaging. Still, it requires a long and laborious analysis, compromising representativeness because it only allows analyzing specific sample sections (Schwaferts *et al.*, 2019).

3.6.3 Chemical characterization of micro- and nanoplastic particles

Optical and spectroscopic techniques are used together for the chemical characterization of microplastic particles, thus confirming the identity of plastic particles through chemical composition analysis after visual identification (Silva *et al.*, 2018). Nowadays, among the techniques used are those mentioned below, and their use will depend on the conditions and characteristics of the sample (Figure 6).

3.6.3.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

Often the microplastics $> 10 \mu\text{m}$ are analyzed qualitatively by FT-IR spectroscopy because they can be identified quickly and directly by comparing the spectra of the polymer with the spectra of known plastics and allowing the identification of the functional groups present (Silva *et al.*, 2018). FT-IR gives a specific absorbance spectrum of the sample by irradiation with infrared light at a defined wavelength, which allows it to identify the sample. With this method, the aging of the polymer can be determined by observing the oxidation of the surface through characteristic bands such as the carbonyl group (Renner *et al.*, 2018).

Furthermore, FT-IR can be applied coupled with total attenuated reflectance (ATR-FT-IR) used in particles $> 500\mu\text{m}$ or coupled with a Focal plane matrix detector (FPA- μ FT-IR) that detects microplastic particles with an approximate resolution of $10\text{-}20\mu\text{m}$ (Huppertsberg & Knepper, 2018). ATR-FT-IR allows the analysis of coarse samples, such as filters/membranes that are not transparent to the infrared. However, it lacks sensitivity and little efficiency in detecting very small microplastic particles (Cincinelli *et al.*, 2017; Pico *et al.*, 2019; Silva *et al.*, 2018). On the other hand, FPA-FT-IR can measure multiple points simultaneously, obtaining the spatial spectra in a matrix of $n \times n$ pixels, where each pixel is an independent IR spectrum. Therefore, small fibers and microplastic fragments can be identified in shorter times compared to techniques that pre-select particles before analysis (Cincinelli *et al.*, 2017; Renner *et al.*, 2018). FPA-FT-IR could provide a high-performance analysis of total microplastics in a sample as it evaluates the spectra of individual particles (Löder *et al.*, 2015). It is also possible to combine FT-IR with AFM,

which allows the recording of chemical images with a spatial resolution below the diffraction limit to obtain information in a range of 50 nm (spectral and spatial) of special samples and specific particles (A. Dazzi *et al.*, 2015; Alexandre Dazzi & Prater, 2017).

3.6.3.2 Raman Micro-spectroscopy (RM)

This method provides a specific vibrational spectrum that unequivocally identifies plastic particles and can use shorter wavelength lasers resulting in a higher spatial resolution (Araujo *et al.*, 2018; K ppler *et al.*, 2016; Ribeiro-Claro *et al.*, 2017), allowing the analysis of microplastic particles up to $1\mu\text{m}$ (Huppertsberg & Knepper, 2018; Imhof *et al.*, 2016; K ppler *et al.*, 2016; Schymanski *et al.*, 2018). K ppler *et al.* (2016) defined Raman spectroscopy as a dispersion method that uses a laser (monochromatic light) to irradiate the sample, which causes energy change of the scattered photons to provide information about the vibrations of the molecules. Raman spectroscopy is one of the most commonly used techniques together with FT-IR since it requires little sample, minimal preparation and it is recommended when dealing with environmental samples.

Moreover, it does not destroy the material and can be considered more respectful of the environment (K ppler *et al.*, 2016; M. Oliveira & Almeida, 2019; Silva *et al.*, 2018). Nevertheless, Raman is not sensitive when it comes to studying the degradation of polymers since variations in the spectra are difficult the identification (M. Oliveira & Almeida, 2019). Furthermore, the degradation of the sample by UV exposure limits the analysis, and fluorescence produces a bad Raman signal (Silva *et al.*, 2018).

Raman microscopes (RM) achieve a submicron resolution because they are confocal. This favors the analysis of individual particles, but identifying a representative number of particles takes several days (Schwaferts *et al.*, 2019). Additionally, RM enables the chemical and morphological characterization of microplastic particles, even when they constitute a small proportion of the sample. This technique is particularly suitable for samples with a low mass and high abundance of microplastic particles (Anger *et al.*, 2018).

Raman Coherent Anti-stokes Dispersion (CARS) and Stimulated Raman Scattering (SRS), non-linear Raman techniques, both have the potential to analyze microplastics as they are not affected by fluorescence, as long as the contaminants are inactive at the frequency of

interest. This reduces the importance of sample preparation, which is crucial for environmental samples (Araujo *et al.*, 2018). Moreover, Raman spectroscopy can be combined with AFM, allowing for imaging with a spatial resolution as high as 10 nm. (Kumar *et al.*, 2015; Yeo *et al.*, 2009).

The improved Raman Spectroscopy Tip (TERS) has been used to explore the interactions of polymer blends in thin films (Yeo *et al.*, 2009). TERS has tips coated with Ag or Au that improve the Raman signal (Kumar *et al.*, 2015). However, organic matter located on the surface of the plastic particle can interfere (Schwaferts *et al.*, 2019). When comparing FT-IR and Raman methods, it has been shown that Raman provides a better response to the non-polar symmetric bonds. At the same time, FT-IR allows better identification of the polar groups, becoming complementary techniques (Silva *et al.*, 2018).

3.6.3.3 Gas Chromatography-Mass Spectrometry (GC-MS)

Another method used to analyze microplastics is the characterization by Mass Spectrometry in combination with Gas Chromatography (GC-MS) which provides information on the mass fraction of the polymer (Schwaferts *et al.*, 2019). This method has variations, such as pyrolysis Py-GC-MS, TED-GC-MS, and TGA-SPE combined with TDS-GC-MS. Therefore, Py-GC-MS is a destructive technique that identifies the polymer and its plastic additives associated (amount of sample ranging from 5 to 200 µg) through the analysis of thermal degradation products (Figure 12).

By means of Py-GC-MS, decomposition products are obtained in an inert atmosphere and separated by a chromatographic column, later identified by their characteristic mass pattern by MS (Dümichen *et al.*, 2015). Nevertheless, Py-GC-MS provides polymer mass per sample but does not allow for the determination of the morphology, type, or number of microplastics. However, it cannot differentiate between the polymer subtypes (Silva *et al.*, 2018). In complex samples, the small amount of sample analyzed may not be representative of the composition, and when samples present high concentrations of impurities and polymers present similar pyrolysis products, this technique is not recommended (Li *et al.*, 2018; Renner *et al.*, 2018; Schwaferts *et al.*, 2019; Silva *et al.*, 2018).

Moreover, TED-GC-MS combines mass spectrometry by thermal desorption gas chromatography with thermogravimetric analysis

(TGA) (Figure 13). This method allows for representative sampling, enabling rapid analysis and quantification of microplastics (up to 100 mg) without requiring preselection or removal of the organic matrix. However, it has high detection limits, necessitating sample preconcentration, and does not provide information on morphology or aggregation (Käppler *et al.*, 2016; Renner *et al.*, 2018; Schwaferts *et al.*, 2019; Silva *et al.*, 2018).

Other methods used for microplastic analyses based on chromatography are High-Temperature Gel Permeation Chromatography (HT-GPC). This method presents better results with particles of known polymers and samples that can be easily cleaned but does not provide information such as size and the number of particles (Käppler *et al.*, 2016). However, shows a better separation of peaks in semi-crystalline polymers (Pico *et al.*, 2019). Additionally, TGA-DSC allows identifying different polymers by differences in their melting characteristics and glass transition temperatures.

Li *et al.* (2018) utilized Liquid Chromatography (LC) to quantify microplastics without the need for a specific size of microplastics. However, this method does not provide information on the morphology and quantity. Furthermore, they pointed out that HPLC can be combined with a size-exclusion system to quantify microplastics. Nevertheless, more studies are needed to verify its efficacy.

3.6.3.4 X-ray photoelectron spectroscopy (XPS)

Magri *et al.*, 2018 utilized a laser ablation technique to produce PET nanoparticles that simulate photodegraded PET nanoparticles. Then, a chemical characterization of the pristine PET and the produced PET nanoparticles was conducted using X-ray photoelectron spectroscopy (XPS). XPS results revealed that the relative O/C ratio of the produced PET nanoparticles increased to 32.1% compared to the 12.3% ratio of pristine PET. This indicates a higher oxidation level in the PET nanoparticle, as determined by the analysis of elemental concentrations. Through XPS, specific characteristic bands of the elements are obtained after irradiating the sample with X-rays. The X-radiation causes the emission of photoelectrons containing information about the binding energy (Schwaferts *et al.*, 2019). An advantage of this method is that it allows observing changes in surface oxidation (Figure 14). However, it cannot unequivocally identify the polymer on its own, so it also becomes a technique complementary to

others (S. Lu *et al.*, 2018; Magri *et al.*, 2018).

3.6.4. Quantification Methods

Many methods proposed in the literature to quantify microplastics are based on visual techniques of particles, making these methods subjective and bias-inductive. However, in recent times, there has been an increase in the number of methods being tested to quantify microplastic and nanoplastic concentration. These methods are being adapted to the challenges and configurations required to analyze this type of particle (Figure 6).

3.6.4.1 Py-GC-MS, TED-GC-MS, TGA-FTIR-MS, and TGA-GC-MS

Fischer & Scholz-Böttcher (2017) proposed a method based on Curie-Point, Py-GC-MS, and thermo-chemistry to simultaneously identify and quantify 8 common polymers (PP, PS, PE, PET, PVC, PA, polycarbonate, and poly methyl methacrylate) (Figure 15). This method can quantify traces of microplastics, but the pyrolysis products must have a consistent composition and require highly reproducible pyrolysis conditions. For the analyses, the method needs an external calibration curve using polymer standards, and then, the programs obtained can be compared with an internal database.

Dümichen *et al.* (2015) pointed out that TED-GC-MS is also an ideal technique for quantifying PE in environmental samples. The concentration is obtained by the percentage of PE weight per gram of the sample. Additionally, the authors mention the TGA-FTIR-MS method, which involves heating the samples and measuring the mass loss as a function of temperature or time (Figure 16).

The decomposition products of polymers are characteristic for each type but are formed at the same temperature (between 350 to 450 °C). Therefore, in order to distinguish between different types of polymers, it is necessary to separate their decomposition products. TGA-FTIR-MS enables measuring weight changes of sample masses up to 100 mg under inert atmospheres. Furthermore, combining TGA and GC-MS can also be convenient since it allows solid phase extraction of the representative part of the decomposition gasses ((Duemichen *et al.*, 2014; Dümichen *et al.*, 2015).

3.6.4.2 High-Temperature Gel Permeation Chromatography (HT-GPC)

HT-GPC was used to characterize and quantify polyolefin microplastics, especially polystyrene, and polypropylene, in samples of personal care products. The study thoroughly analyzed the size, shape, molecular weight distribution, and stabilization of polymer particles. The mobile phase utilized in this method was 1,2,4-Trichlorobenzene, and the calibration was performed using PP standards (Hintersteiner *et al.*, 2015). The method demonstrated a high recovery rate from 92% to 96%.

3.6.4.3 Thermal Analysis Techniques (TA)

According to Rodríguez Chialanza *et al.* (2018), these techniques, which include Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC), measure fundamental thermodynamic properties such as enthalpies, thermal capacities, and phase transition temperatures, which are characteristics for each plastics material (Figure 17). These techniques commonly study plastic samples such as PE, PP, and PET since they are semi-crystalline materials with different melting temperatures, allowing their identification and quantification. However, they are not specific when the sample is a mixture of microplastics with near melting points (Majewsky *et al.*, 2016). For the quantification, it is necessary to elaborate calibration curves for each plastic particle of interest (Rodríguez Chialanza *et al.*, 2018).

3.6.4.4 Visible - Near-infrared spectroscopy (Vis-NIR)

Another method used for the quantification of microplastics is near-infrared spectroscopy. Corradini *et al.* (2019) used this method to quantify microplastics in soil samples, mainly PE, PET, and PVC. Calibration curves were prepared with reference polymers for the analyses, and fast results were obtained since the method analyzes solid samples without the need to extract plastic particles. Additionally, NOAA proposes a gravimetric analysis to quantify plastic particles (Masura *et al.*, 2015).

4. Discussions

Even though different techniques have become useful tools for the detection of micro- and nanoplastic in the environment, there is still potential for significant development and more efficient analytical methodologies for this purpose. The future trends may focus on: a) in-depth

studies of the degradation process of polymeric materials and how they interact, sorb, and transport chemical pollutants on their surface, b) while some studies have created databases for commonly weathered and degraded microplastics such as PE, PP, PET, PS, and PA, there is still a need for databases of micro- and nanoplastics with more complex compositions, c) standardize the units of measurement for the concentration of micro- and nanoplastics and determine at what concentrations these particles represent greater risks to environmental and human health.

5. CONCLUSIONS

In this review, we have provided an overview of the occurrence of micro- and nanoplastics, their composition and classification, contamination levels, and the main adsorption mechanisms on solid surfaces, and also, provided a compilation of the main analytical methodologies used for the characterization and quantification of micro- and nanoplastics. This study demonstrates that numerous techniques are being modified to characterize micro- and nanoparticles. However, standardizing analysis methodologies has proven challenging due to the diverse nature of these particles and their nanometer-scale size.

Consequently, morphology, degradation level, and environmental interferences require specific configurations for analyzing micro- and nanoparticles. Specifically, size and mass represent a challenge because many analytical techniques are limited by the detection limit or its spatial resolutions.

Measures and regulations have been implemented in developed countries regarding the use, recycling, and disposal of plastic waste. However, inadequate disposal of plastic waste persists and is more noticeable in underdeveloped or unregulated countries. Therefore, more efficient measures must be proposed and implemented to address this issue, and it is necessary to raise awareness among the population regarding the proper disposal of plastic waste.

6. DECLARATIONS

6.1. Study Limitations

The study is limited to the sources used in the research.

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6.4. Competing Interests

The authors declare no conflict of interests.

6.5. Open Access

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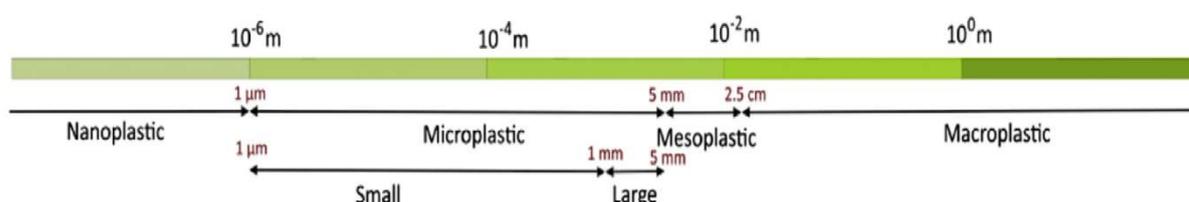


Figure 1. Plastic debris nomenclature based on size. Reproduced from Van Cauwenberghe *et al.* (2015).

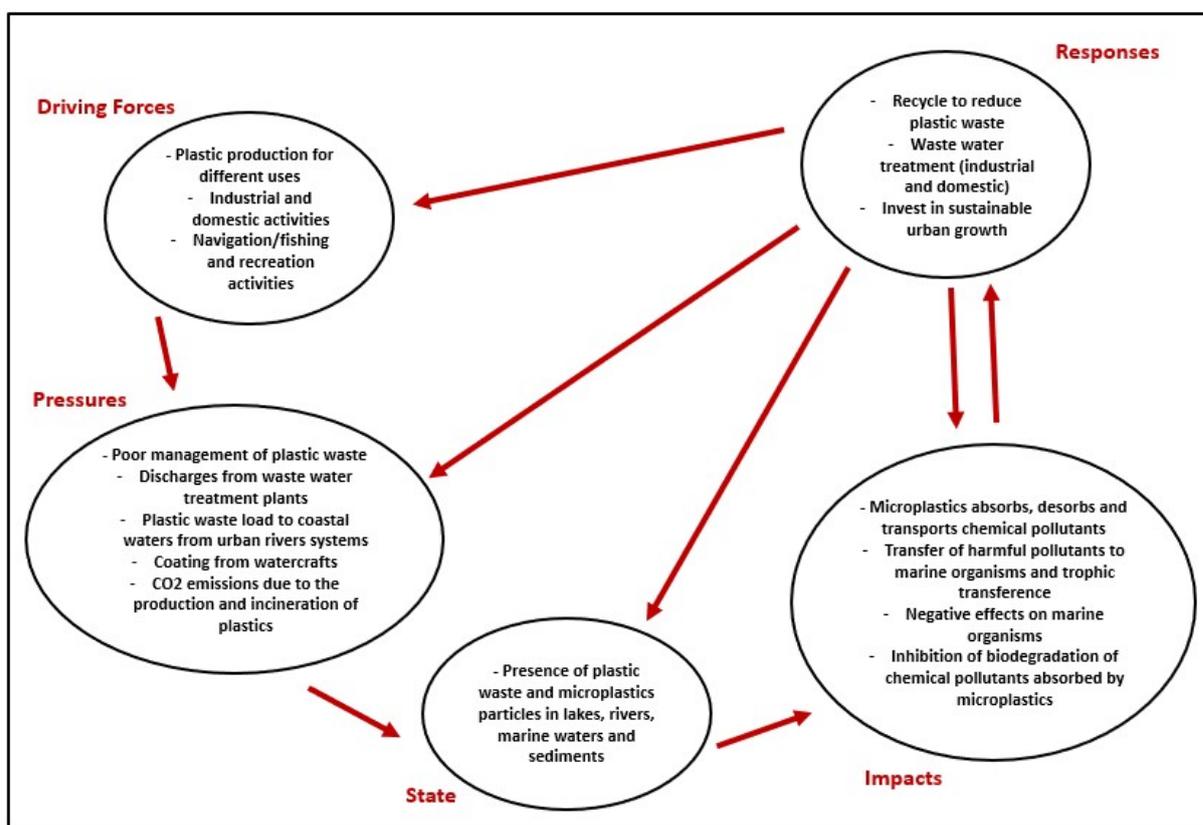


Figure 2. DPSIR framework for assessing the sources and fate of microplastic pollution. Reproduced from Nolasco *et al.* (2022).

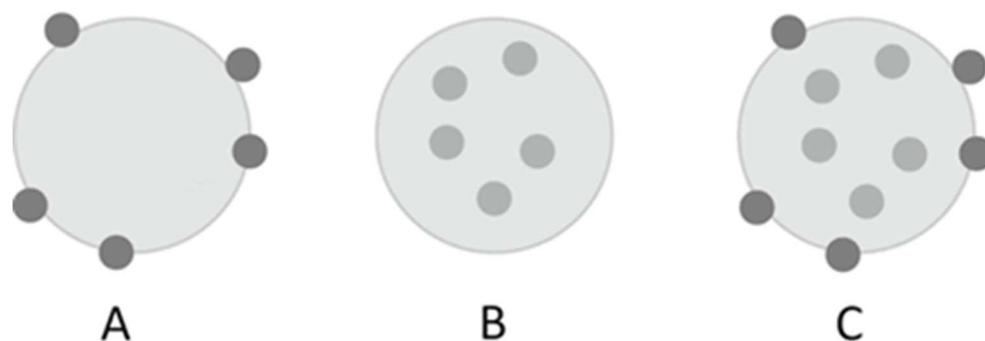


Figure 3. Illustration of the difference between (a) adsorption (b) absorption and (c) combination of ab- and adsorption processes. *Reproduced with permission from Springer Open (Rist and Hartmann 2018).*

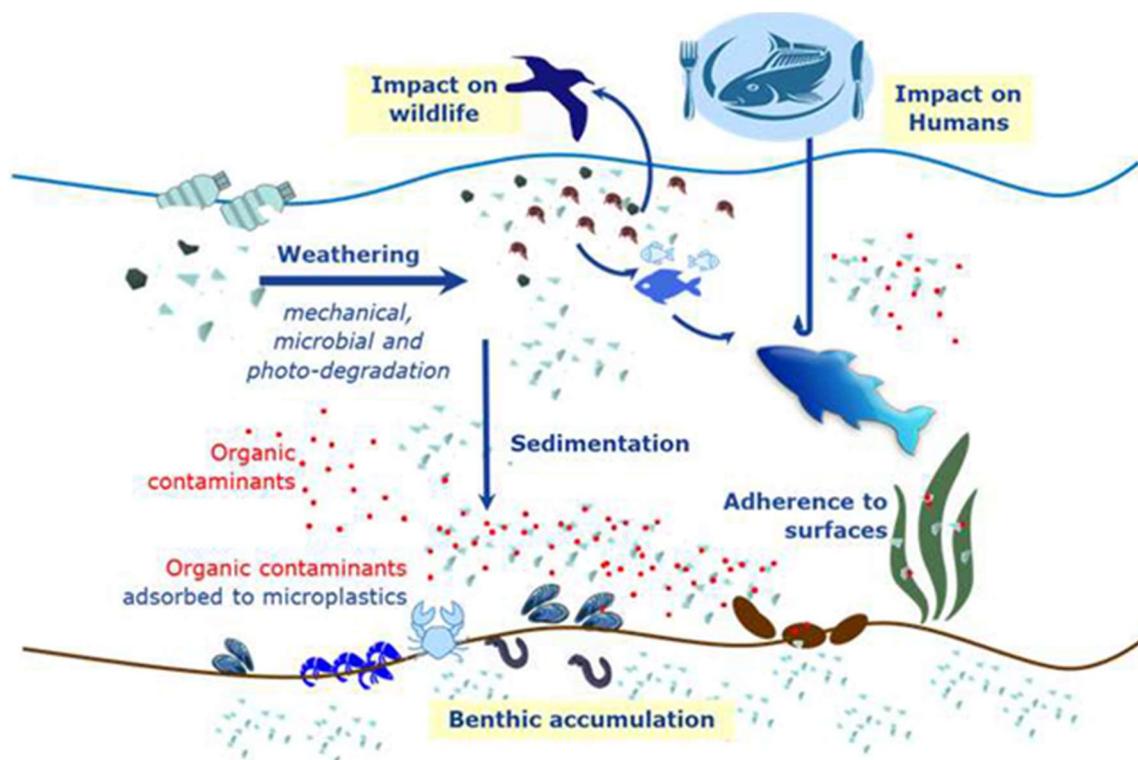


Figure 4. Schematic representation of how microplastics enter in the food-cycle. *Reproduced with permission from Joint Research Center (Munoz-Pineiro 2018).*

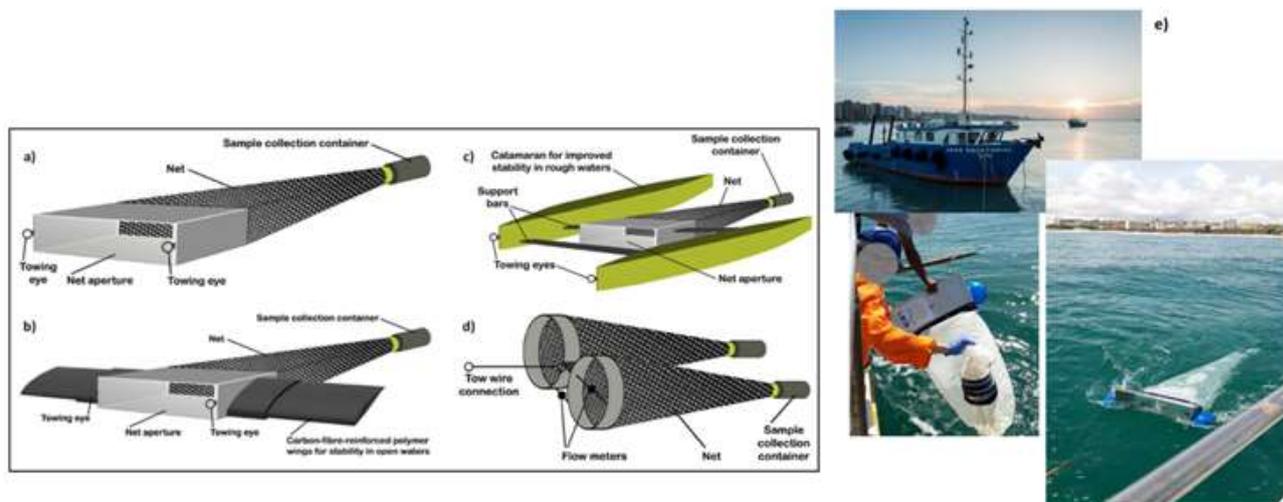


Figure 5. Types of equipment for sampling microplastics in surface seawater: a) neuston net, b) manta trawl, and, c) catamaran, as well as in mid-water level d) bongo nets (Reproduced from Silva *et al.* 2018) and e) Self-made neuston sampler (Reproduced from Nolascoet *al.* 2022).

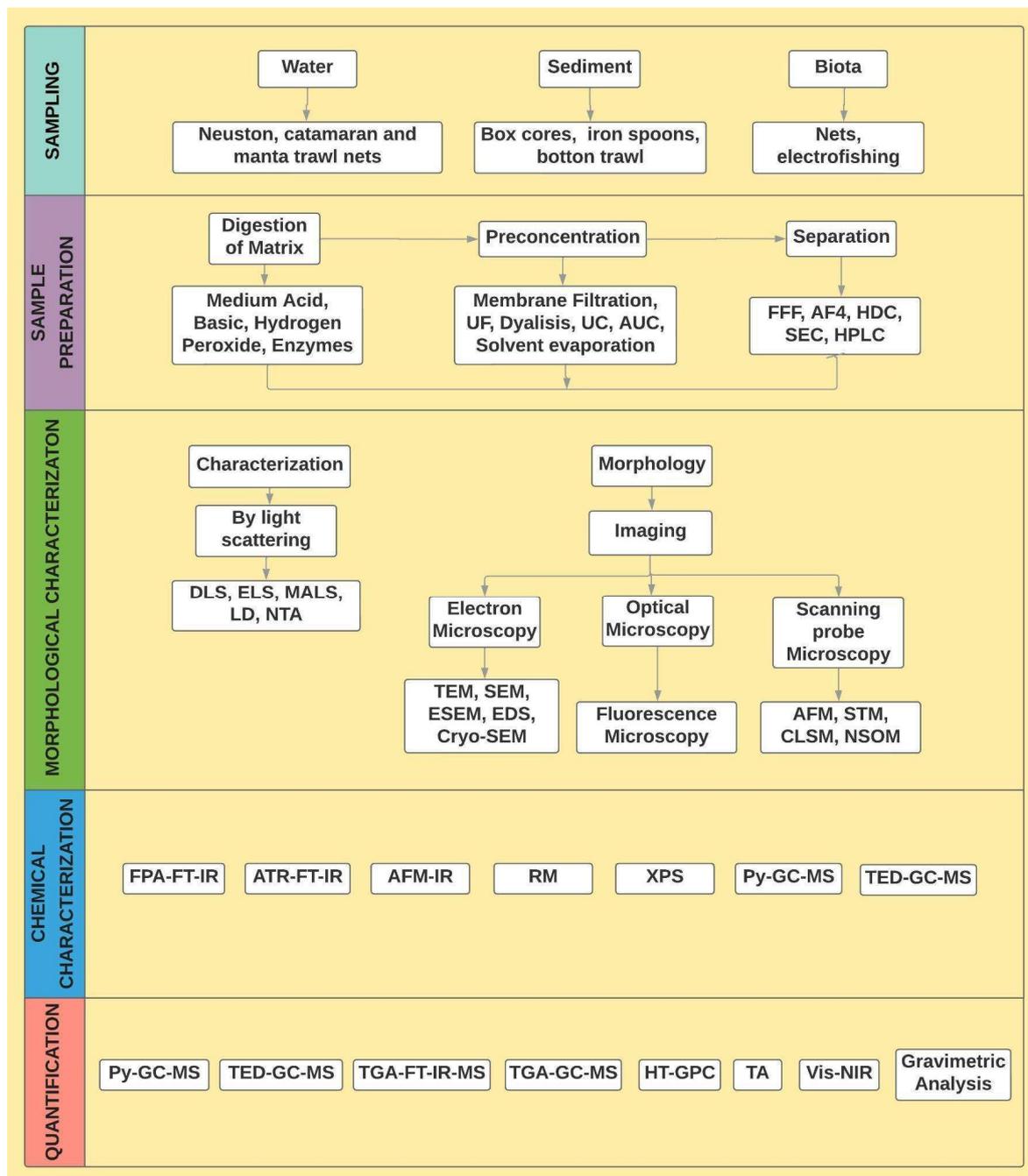


Figure 6. Possible methods used for the analysis of micro/nanoplastic in different types of samples separated by sampling, sample preparation, morphological and chemical characterization and quantification (adapted from Pico, Alfarhan, and Barcelo 2019).

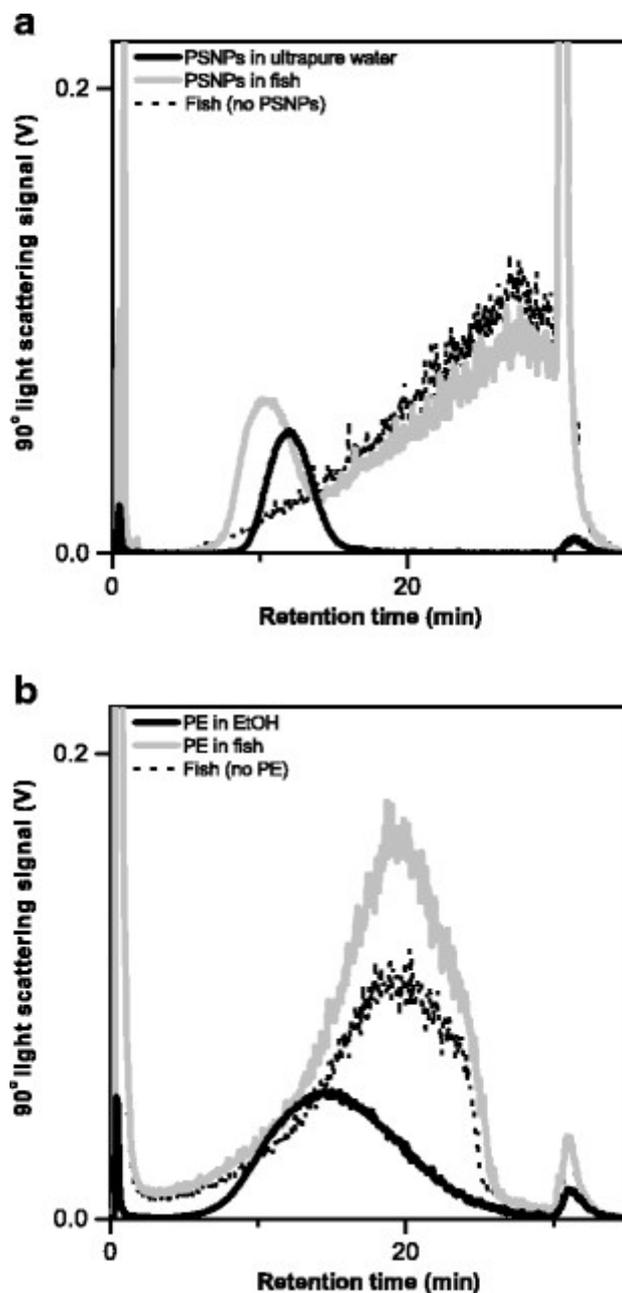


Figure 7. AF4-LS results obtained for PS nanoparticles (a) and PE particles (b) in fish using 0.025% (v/v) FL-70 as a carrier liquid. For comparison, the fractograms acquired for the pristine PSNPs and PE particles and the non-spiked fish are shown. This figure is reproduced from Correia and Loeschner (2018).

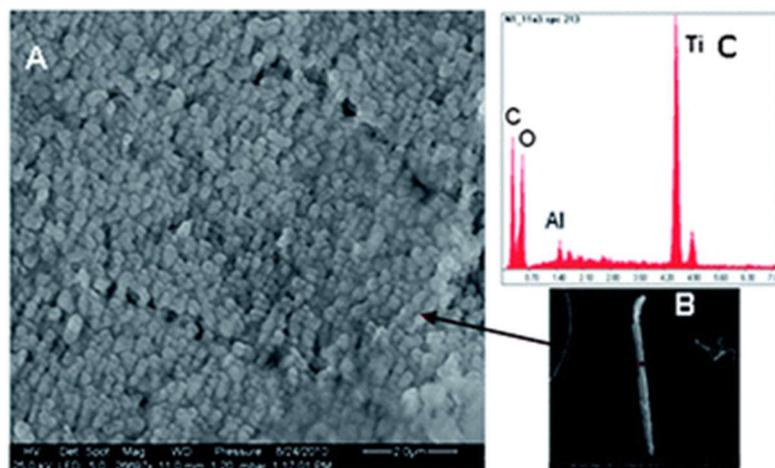


Figure 8. (A and B) SEM images of particle x. (C) EDX spectra showing high titanium (Ti) content, not specified plastic carbon (C) and oxygen (O). This figure is reproduced from Fries *et al.* (2013).

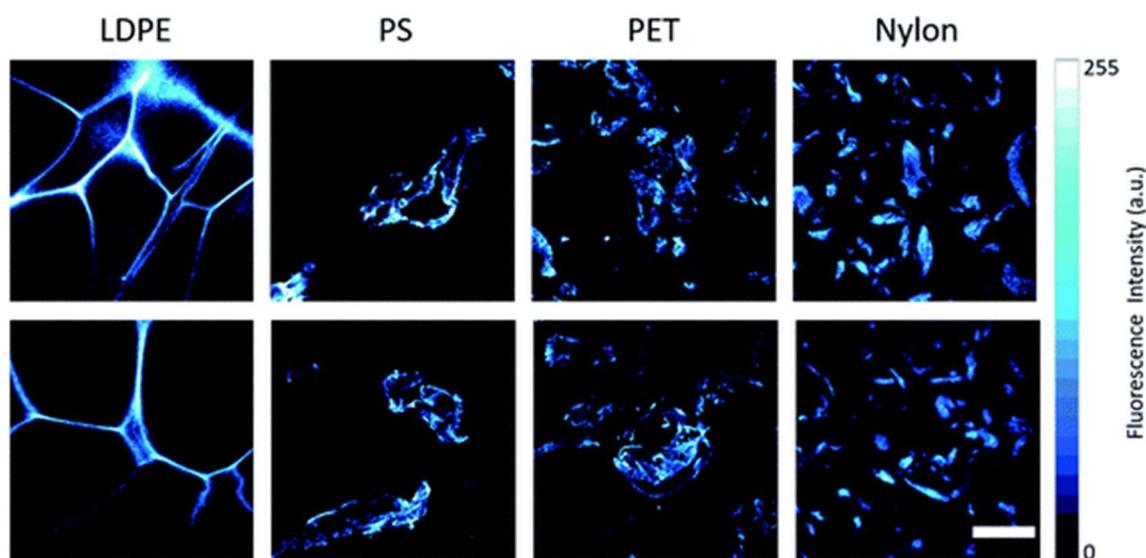


Figure 9. Representative confocal fluorescence microscopy images of microplastics dispersed in water and stained with Nile Red. From left to right: LDPE, PS, PET, and nylon. The scale bar is 200 μm . This figure is reproduced from Sancataldo *et al.* (2020).

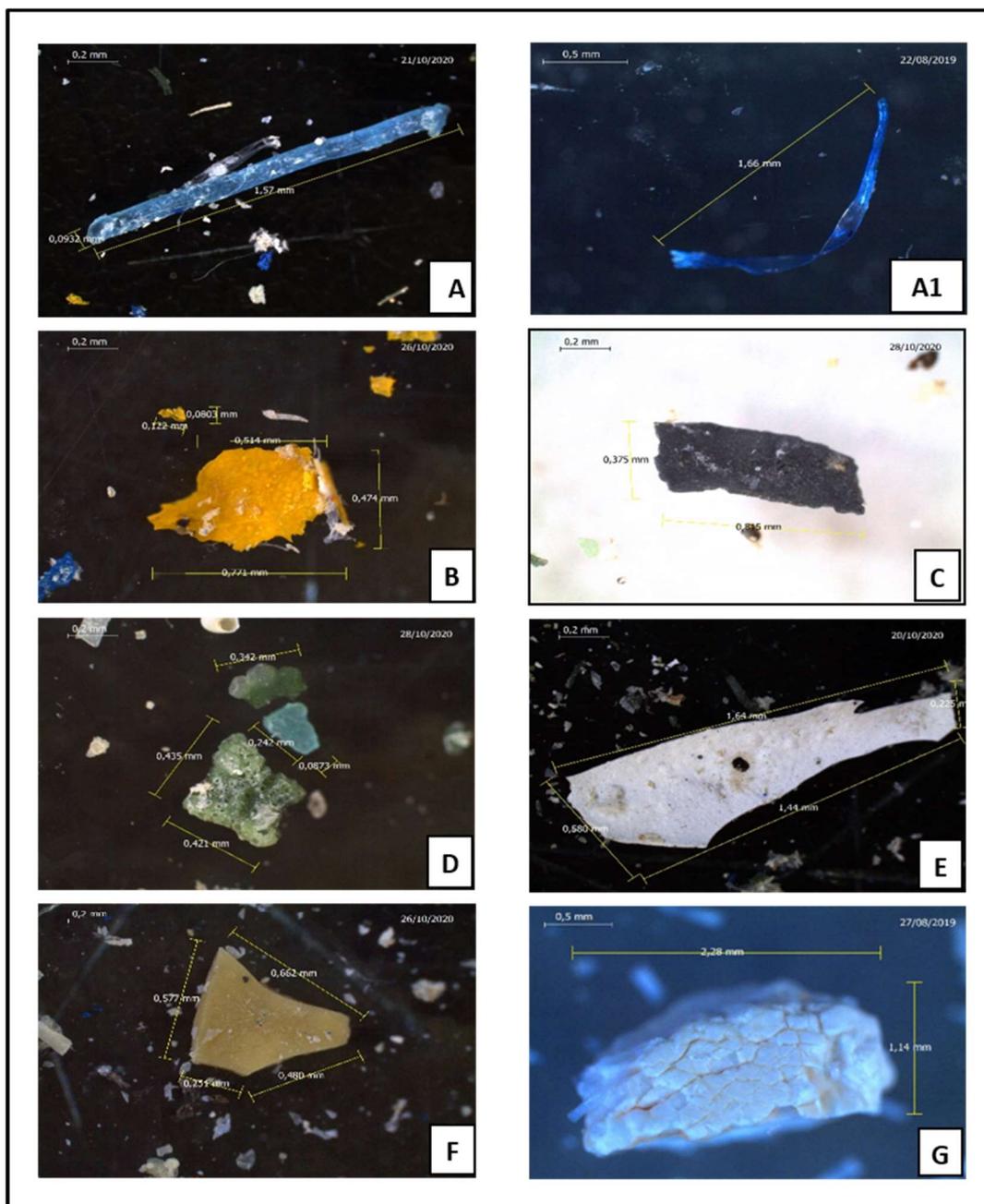


Figure 10. Different microplastic particles morphologically characterized using a stereoscopic microscope. This figure is reproduced from Nolasco *et al* 2022.

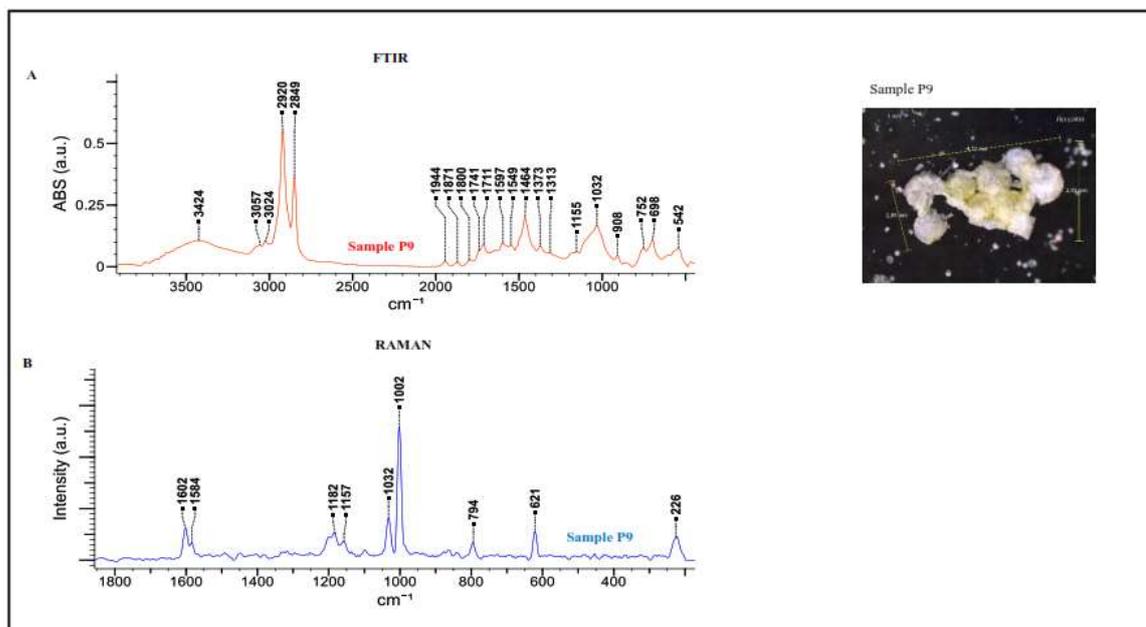


Figure 11. FTIR and Raman spectra of a PS microparticle. This figure is reproduced from supplementary information from Nolasco *et al* 2022.

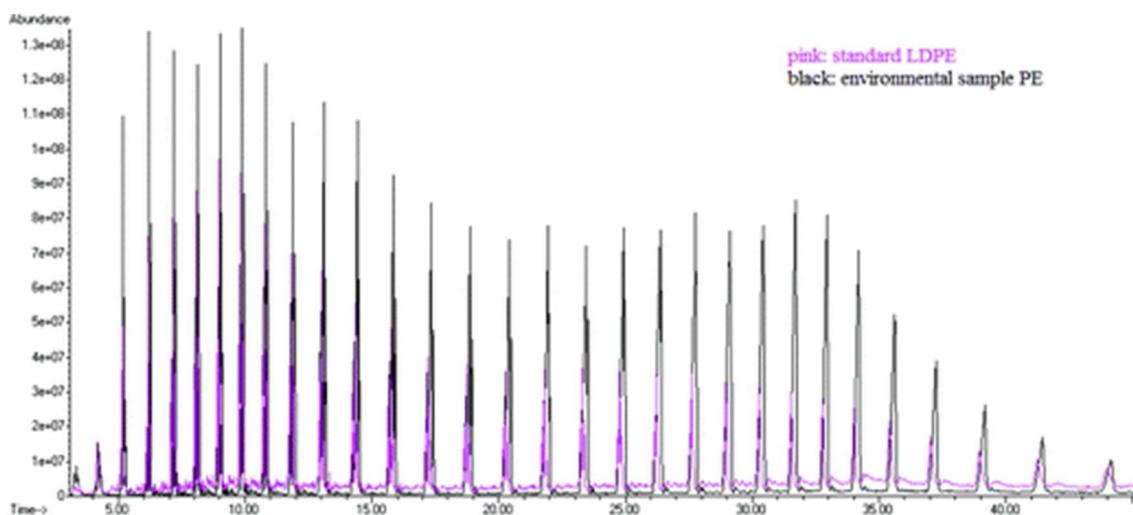


Figure 12. Pyrogram of PE (black) found in the environmental microplastic overlaid by the pyrogram of a PE standard (pink). This figure is reproduced from Fries *et al.* (2013).

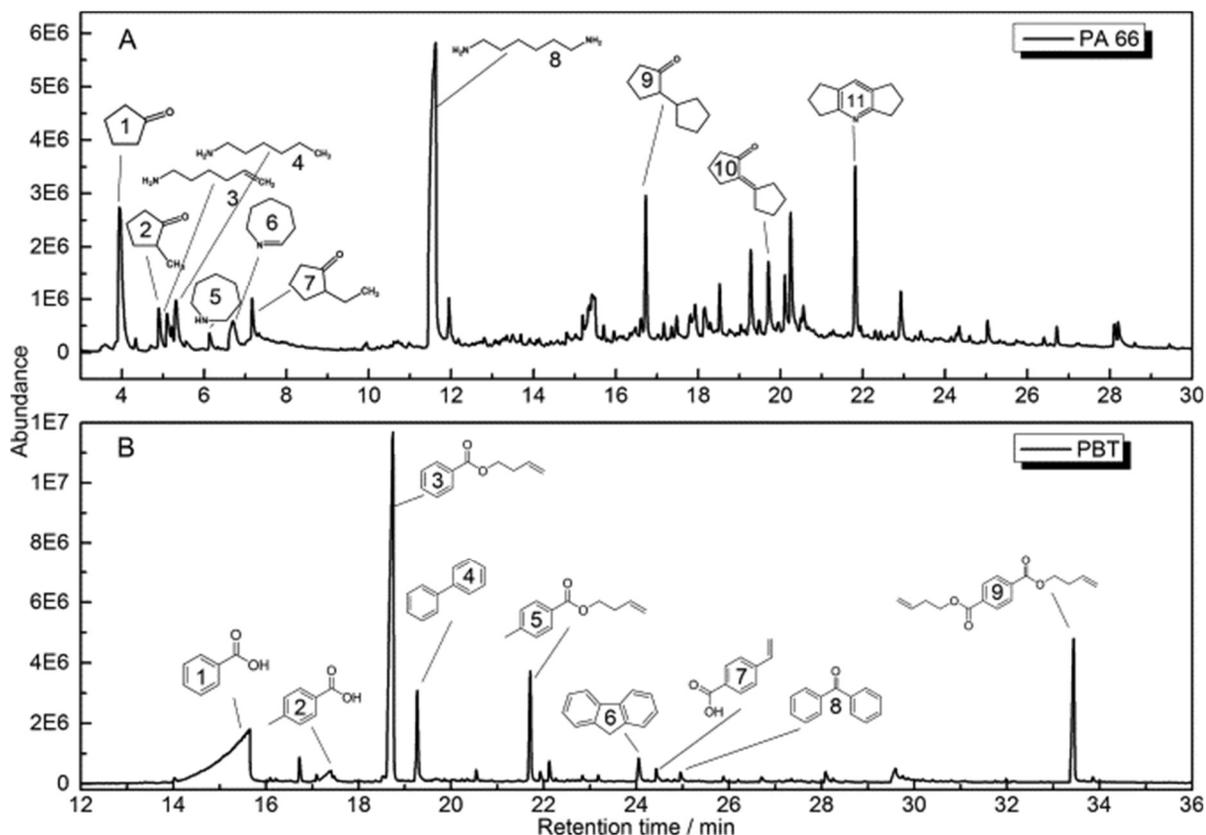


Figure 13. Chromatograms of PA 66 (A) and PBT (B), measured with TGA–SPE/TDS–GC–MS by using an HP-1MS column, a sample mass of 2 mg and a purge gas flow (TGA) of 30 mL min⁻¹. This figure is reproduced from Duemichenet *al.* (2014).

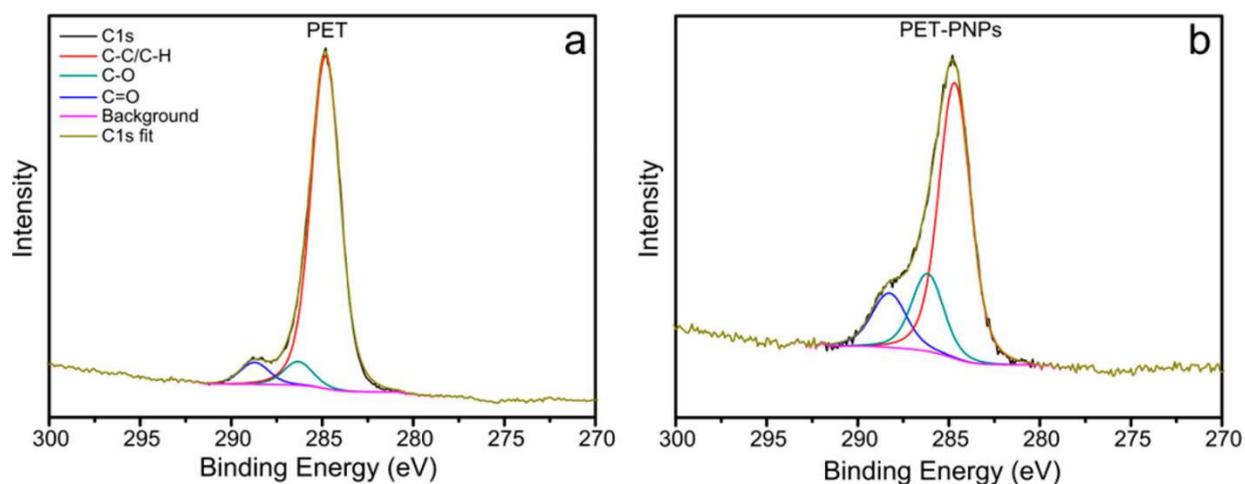


Figure 14. XPS characterization. XPS C1s high-resolution spectra of the pristine PET (a) and of the as-synthesized PET PNPs (b). This figure is reproduced from Magrièr *al.* (2018).

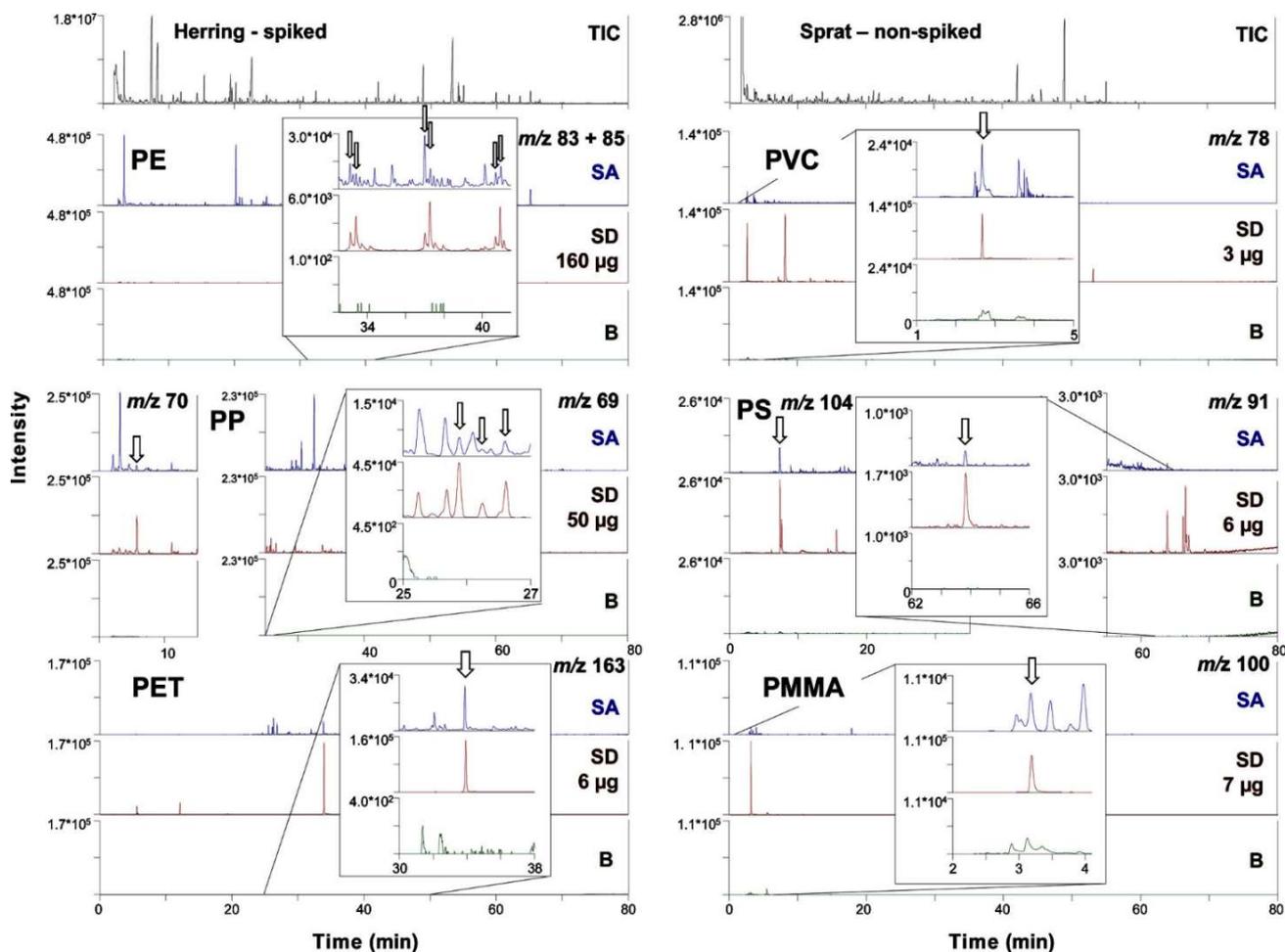


Figure 15. Total ion chromatograms (TIC) of a spiked and a nonspiked MP fish sample. Left column: Herring sample, spiked with PE, PP, and PET; right column: Sprat sample nonspiked. Polymer indicator ion chromatograms of samples (SA, blue), respective standard mixtures (SD, red) and procedural blanks (B, green). Sections of interest are enlarged. This figure is reproduced from Fischer & Scholz-Böttcher (2017).

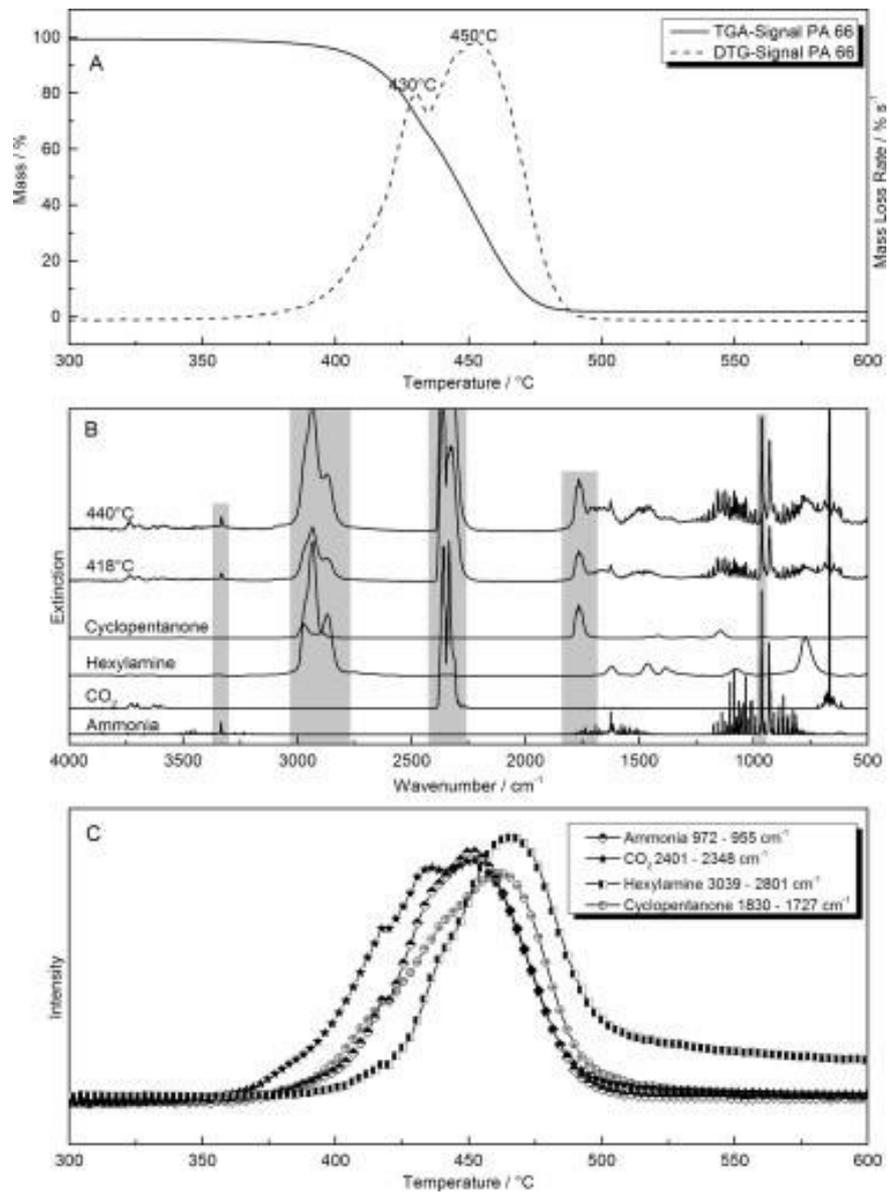


Figure 16. (A) Thermogram and DTG signal of PA 66; (B) spectra of the main decomposition steps of PA 66 in comparison to reference spectra; (C) product release rates of the main degradation products of PA 66, measured with TGA-FTIR. This figure is reproduced from Duemichenet *al.* (2014).

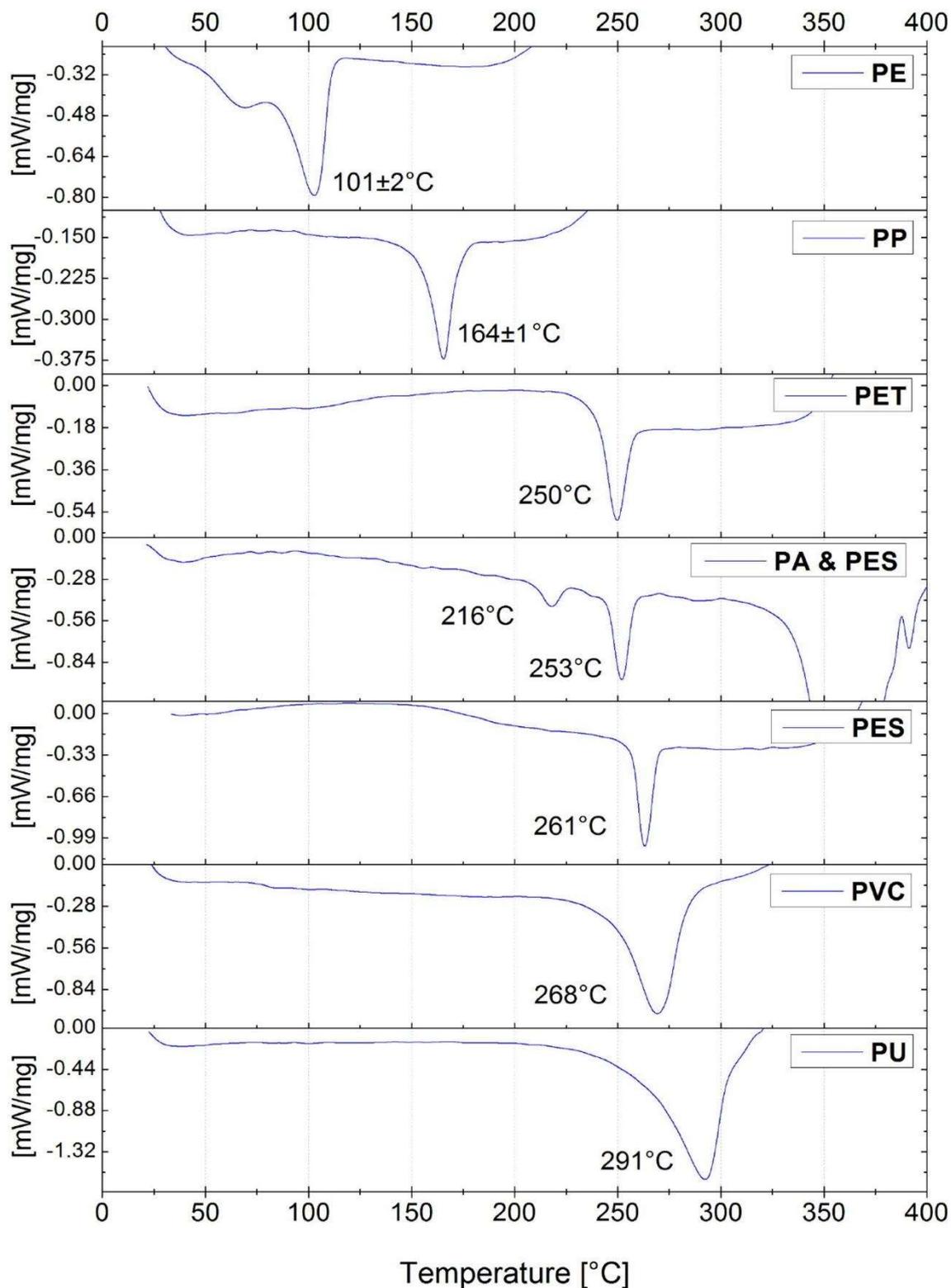


Figure 17. Endothermic phase transition heat flows and peak temperatures of LDPE, PP, PET, polyester (PES), PA, PVC and polyurethane (PU) using TGA-DSC; heating rate 5 K min^{-1} under nitrogen atmosphere; peak melting temperature given as arithmetic mean \pm one standard deviation. This figure is reproduced from Majewsky *et al.* (2016).