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Interaction of microplastics with metal(oid)s in aquatic environments: What is done so far?

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ABSTRACT

Microplastics (MPs) are being recognized as an emergent route of contaminants to aquatic environments, which initially attracted the research interest on their interactions with organic pollutants. Lately, a turning point of attention is evident, with more published studies reporting the presence of metal(oid)s in plastics. This review assembles the mechanisms occurring on microplastics surfaces that enhance sorption of hazardous elements (i.e., metals and metalloids) over environmental exposure. Reported findings of experimental studies are of major importance to understand the factors controlling the sorption/desorption of metal(oid)s to/from microplastics as much as determination of metal(oid)s in environmental plastics. Existence or formation of oxygen-containing functional groups and complexes from surface coatings strongly allow bond of metal(oid)s on reactive surfaces while sorption dynamics are strongly controlled by water chemistry parameters. Moreover, the present work evidences the potential impacts caused by metal(oid)s-MPs interactions to aquatic organisms, prioritizing the need of environmental realistic parameters to test. Bioaccumulation of metal(oid)s desorbed from ingested MPs prove the significant influence of these plastic particles in the bioavailability of pollutants to aquatic biota. In this way, this is a comprehensive manuscript committed to the estimation of the potential ecological risk of MPs to aquatic environments due to their association with metal(oid)s.

1. Introduction

Land- based plastic debris are considered a problem of marine pollution, composing about 80% of the marine litter (GESAMP, 2015, GESAMP, 2019; UNEP, 2016; Plastics Europe, 2017). In addition to land sources, over than 11,000 tons of ALDFG (Abandoned, Lost and Discarded Fishing Gear) and marine accidents that lose containers transporting plastic pellets are contributing to annual numbers of plastic waste in Europe (GESAMP, 2019). Plastics are synthetic polymers produced from organic materials such as fossil fuels, or by bio-based feedstocks, which are widely applied in routine industries as food packaging or personal care products. According to their size, microplastics (MPs) are plastics ranging from 100 nm to 5 mm. They can be divided into primary (originally produced with this size for several purposes) or secondary microplastics which represent fragmented plastics arising from the effect of environmental conditions (e.g., photo-oxidation, wave action) that promote their degradation (Andrady, 2017). Despite the non-establishment of an acknowledged quantity of MPs present at regional or global scale, due to the lack of data or studies giving reliable concentrations, coastal environments usually host a higher amount of plastic debris (estimated values of 1–100,000 particles per m^3) than open ocean waters (Norén and Naustvoll, 2010; Wright et al., 2013). As distinctively ubiquitous and small, MPs can enter on biogeochemical cycles and food webs, spreading from surface layer of coastal waters to the sediment compartment of the open ocean (Rogers et al., 2020).

The role of metal(oid)s as harmful to human health is of global knowledge. Being potential toxic elements, metal(oid)s can cause carcinogenic, teratogenic and allergenic effects (Cooksey, 2012; Yang et al., 2015), as well as to induce alterations in behavior and at neurological level (Tchounwou et al., 2014; Koller and Saleh, 2018). Some metals as chromium (Cr), nickel (Ni), cadmium (Cd), cobalt (Co) and lead (Pb) and a very toxic metalloid arsenic (As) represent potential carcinogenic elements that are commonly found in drinking water (Fakhri et al., 2018). The persistence, bioaccumulation and high toxicity of this hazardous substances make them a serious threat to environments. These elements can be found in aquatic environments as a result of leaching from metal-based materials, farming or mining, introduced through wastewater effluents (Förstner, 1980; Deheyn and Latz, 2006; Almeida and Sousa, 2007; Brennecke et al., 2016; Koller and Saleh, 2018; Barletta et al., 2019). On its ionic

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form, metal(oid)s can have a great affinity by dissolved organic matter (Santos-Echeandia et al., 2008b) strongly present in media, or different anions (e.g., carbonates, chlorides, hydroxides) (Millero, 2001).

The increasing awareness about the presence of MPs in the aquatic environment has highlighted to warning consequences concerning ecosystem's health (Brennecke et al., 2016). Physical impact is inflicted on marine species of different trophic levels as a result of their direct contact with these small pieces in their natural environments (Wright et al., 2013). However, this is not the only implication caused by the spread of MPs in nature, since they contain or can interact with other pollutants (i.e., metals, metalloids), resulting in a chemical impact beyond the physical damage (Roman et al., 2020). The transfer of contaminants from MPs to the tissues of organisms has been already reported, potentially causing increased concentrations and toxicological effects on aquatic biota (GESAMP, 2015; Luís et al., 2015; Barletta et al., 2019; Rivera-Hernández et al., 2019). Plastics are produced with the addition of organic and inorganic components, acting as plasticizers, stabilizers, surface modifiers, flame retardants, or pigments. Alternatively, these contaminants can also be later associated with plastics by their sorption from the surrounding water once in the environment (Town et al., 2018; Santos-Echeandía et al., 2020). The essential features that guide the processes of sorption and desorption occurring between a microplastic particle and a pollutant are mediated by their chemical and physical characteristics, with abiotic parameters having a key-role in this process (Rodrigues et al., 2019). To understand this phenomenon, studies frequently focus on the comparison of the amount of elements accumulated on MPs represented by virgin plastic particles and the ones collected from the environment, often resorting to pellets (Ashton et al., 2010; Holmes et al., 2014; Rochman et al., 2014; Fisner et al., 2017; Vedolin et al., 2017; Munier and Bendell, 2018; Gao et al., 2019) or small fragments (Brennecke et al., 2016; Santos-Echeandía et al., 2020; Wang et al., 2020). Accordingly, metal(oid)s can be transported to and between aquatic environments through their interaction with MPs (Akhbarizadeh et al., 2016; Wang et al., 2016; Vedolin et al., 2017). As representants of potential hazardous substances, the reduction of metal concentrations in the environment is the aim of environmental protection agencies and European Directives such as the WFD (2000/60/CE) and the MSFD (2008/56/CE). Wherefore, the emergent route of metal(oid)s to aquatic environments through MPs as vehicles deserves global attention. Nonetheless, to date, organic compounds have been greater explored regarding the impact of their interaction with MPs to environmental contamination, probably due to the hydrophobic trait in common (Antunes et al., 2013; Ferretto et al., 2014; Pittura et al., 2018; Endo and Koelmans, 2016; Rodrigues et al., 2019). A turning point has been observed in the last years, as more studies investigating interactions with metal(oid)s have been published (Akhbarizadeh et al., 2016; Brennecke et al., 2016; Wang et al., 2016; Vedolin et al., 2017; Dobaradaran et al., 2018; Lu et al., 2018; Maršić-Lučić et al., 2018; Munier and Bendell, 2018; Town et al., 2018; Acosta-coley et al., 2019; Gao et al., 2019; Mohsen et al., 2019; Richard et al., 2019). However, overall mechanisms and factors involved in the metal(oid)s-MPs interactions have not been well enlightened to date.

The present manuscript is a critical evaluation of the current state of investigation concerning the interaction of microplastics with metal(oid)s in the aquatic environment. Despite a few reviews have been published regarding the interactions of MPs with metals, this the first one including both metals and metalloids, specifically. Available published research, essentially from the last 6 years, was reunited and well detailed here, focused on the mechanisms and circumstances allowing sorption/desorption of these metallic pollutants on/from polymers with emphasis on the modifications occurring in the MPs surface, particularly over environmental exposure. More than that, we enlighten all the possible scenarios reported with organisms to estimate ecological impacts of metal(oid)s-MPs interactions, from bioaccumulation to toxicity effects as a result of their coexposure or estimation through physiologically simulated extraction tests. In this way, this review will provide an insight on the impact of MPs to marine pollution and potential ecological risk due to their interaction with metal(oid)s.

2. Sorption of metal(oid)s on microplastics in aquatic environment

2.1. Surface modification promoting adsorption

Studies carried out since the 1960s demonstrated the tendency of metals to adsorb on plastic surfaces (Robertson, 1968; Struempler, 1973; Good and Schroder, 1984; Grossmann et al., 1990; Giusti et al., 1994; Weijuan et al., 2001; Cobelo-Garcia et al., 2007; Fischer et al., 2007). Even so, the research interest in order to understand their association has been recently globally triggered. The early lack of investigation on metal(oid)s, regarding the interactions of polymers with contaminants could be explained by the scepticism to look on the possibility of metal(oid)s adsorption onto plastic from water. Overall, plastic particles were considered biochemically inert in relation to aqueous metal ions (European Commission, 2019), due to neutral charge of polymers. However, this prior believe was demystified, since their interaction can be feasible (Turner and Holmes, 2015; Rivera-Hernández et al., 2019; Dong et al., 2020; Fernández et al., 2020; Wang et al., 2021) when the particles are suspended in water, allowing them to acquire charge. The MPs-metal(oid)s binding can even be enhanced as plastic properties are modified, mainly driven by environmental processes (weathering) (Santos-Echeandía et al., 2020), or artificially (oxidized MPs), conferring a new more reactive surface to polymers (Wang et al., 2020). Environmental action promotes surface degradation through mechanical, chemical, and biological activities which are fundamentally responsible for structural changes on the polymer (Fig. 1). First, mechanical action (sand abrasion and washing over wave transportation) induce fragmentation of plastic debris introducing surface modification. The decrease of size leads to increase of specific surface area, and more cavities are created, enhancing polymer porosity and conferring a higher roughness ideal to uptake of metal(oid)s (van Leeuwen et al., 2013; Brennecke et al., 2016; Town et al., 2018). Apart from this, the formation of coatings of hydrogenous and biogenic nature (Brennecke et al., 2016; Richard et al., 2019) on the surface of polymers allow adhesion of organic matter (Turner and Holmes, 2015); agglomerates of mineral nature, as silt and clay suspended particles (Johansen et al., 2018); and microbial colonization forming biofilms (Tien and Chen, 2013). The formation of superficial complexes would act as an enhancer to allow interaction with hydrous oxides (which interfere on cation-exchange) and metal/metalloid ions. Such hydrogenous-biogenic coatings occur through formation of metallic oxides on the surface of polymers which promote co-precipitation of metal(oid)s with iron (Fe) and manganese (Mn) oxo-hydroxides (Leiser et al., 2020). Additionally, coatings (i.e., biofilms) also have the capacity to sink MPs, finally reaching the sed-

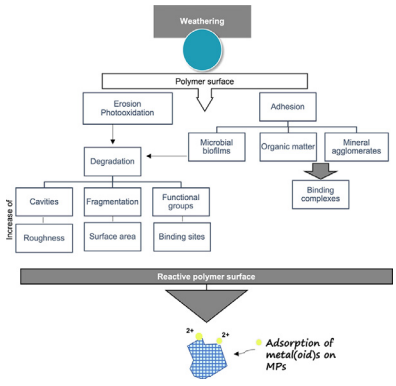

Fig. 1. Summary of surface changes of polymers as a result from weathering that allow adsorption of metal(oid)s on microplastics.

iments, preventing low density polymers from being restricted to the water surface and dragging them to bottom waters. This trip through the water column allows a greater interaction of the polymers with the metal(oid)s present in the water and on the sedimentary matrix. Alternatively, biofilm growing and organic blooms over buoyant polymers may block the UV oxidation reactions (Weinstein et al., 2016; Oberbeckmann et al., 2018; Acosta-coley et al., 2019), also influencing sorption performances. Chemical degradation (mainly hydrolysis) induces modification with creation of new functional groups on the surface of polymers. This occur through breakdown of structural linkages, setting up instable groups able to react with aqueous metal(oid)s (Yu et al., 2019). This polar functional groups usually consist in esters, keto groups and quinone-related structures (Yu et al., 2019; Santos-Echeandía et al., 2020). Besides this, oxygen-based functional groups (OH, C–O and C–OH) created by UV degradation are also essential to metal(oid)ds-polymer bond (Liu et al., 2019; Yu et al., 2019). Biological degradation, as a result of microbial communities fouling over MPs can also modify functional groups. In fact, polarity and electronegativity of polymers are determined by the diversity of functional groups whom create anionic binding sites suitable for the uptake of cations from water (Holmes et al., 2012, 2014; Santos-Echeandía et al., 2020). Consequently, as active sites environmentally created can be limited, metal/metalloid species present at the surrounding environment can compete for binding sites (Yang et al., 2019). In the end, once a metal/metalloid is bound to a functional group, they can increase their stability in the particle surface (Kochanke et al., 2019).

As each polymer type has its own structure, this feature is also important to define adsorption capacities towards metal(oid)s. Despite polymers are essentially apolar, Polyvinyl chloride (PVC) and Chlorinated polyethylene (CPE) have chlorine on their structure which corresponds to one of the most electronegative atoms, so chlorine based functional groups provide polar regions to form a strong bond with metal(oid)s, before or after environmental exposure (Zou et al., 2020). For example, under influence of electrostatic attraction (i.e., high water pH), new polystyrene (PS) MPs exhibit negative charge which promotes the bond of positively charged ions, even before surface alterations through weathering (Mao et al., 2020). Even more, when a polymer is surface modified during the manufacturing process (i.e., oxidized MPs) its sorption capacity can be strengthened, even before suffering from environmental action (Wang et al., 2021). This is allowed by the changes in the superficial functional groups, enhancing the bond with different chemical species.

MPs color appears to be also important since different colors have been associated with different species of metal(oid)s, according to degradation-color relation of environmental polymers (Filella and Turner, 2018; Acosta-Coley et al., 2019). Wang et al. (2016) reported high concentration of metals in dark colors of plastic (bags and screw caps), over hundred times higher than in lighter ones. As matter of fact, darker pellets collected from environment have been associated to MPs that have suffered significant weathering (Fisner et al., 2017; Acosta-Coley et al., 2019; Santos-Echeandía et al., 2020). However, the association of colored polymers with certain metal(oid)s could be due to their use as additives, demonstrating a pigmentation-color relation as well, later discussed on this paper (Section 3).

In brief, polymers have determined properties which can be modified through biotic and abiotic degradation (e.g., functional groups). The match of their unique traits will determine the level of interaction with metal(oid)s and the strength of bindings that will occur in aquatic environments (Min et al., 2020).

2.2. Dynamics of adsorption/desorption influenced by environmental parameters

To investigate interactions of MPs with metal and metalloid ions, studies perform analysis of sorption kinetics, with estimation of sorption efficiencies and mechanisms involved in the process. Primarily, an efficient increase of adsorption of metal(oid)s onto surfaces is frequently observed until equilibrium time is normally reached over 24 (Lin et al., 2021; Wang et al., 2021) or 48 h (Mao et al., 2020; Xue et al., 2021) up to 96 h (Wang et al., 2020) on an aqueous solution (Turner and Holmes, 2015; Fernández et al., 2020; Mao et al., 2020; Tang et al., 2020; Zou et al., 2020). This behavior follows stabilization, which depends on the conditions involved. Regarding desorption, the diffusion of metal(oid)s from polymers towards water can stabilize within 10 h (Tang et al., 2020). Metal ions diffuse into or out of a polymer saturated with water, being partially hydrated, and their rate of release is equal to their diffusion rate in the aqueous media (Reuvers et al., 2015; Town et al., 2018). Town et al., 2018 described a simple model, based on spherical geometry, to explain the description of release kinetics of metal species from nano- and micro-plastic particles, highlighting that is not comparable the velocity and effusion of metal ions in water to metals within polymers. For micro(nano)plastics and metals, the researchers acknowledged the size of the particles and the timescale of the exposure as the main responsible parameters for the dynamics of their relation (Town et al., 2018). Despite equilibrium time in the laboratory studies is normally relatively low (48 to 100 h) (Holmes et al., 2012; 2015), for field studies this scenario can change. In the study of Rochman et al. (2014) it took more than 12 months to achieve equilibrium between metals and microplastic pellets. It is expectable that equilibrium be faster in the controlled conditions of a laboratory experiment comparing to an environment much more dynamic and even unpredictable. Essentially, water chemistry parameters and other conditions from surroundings will dictate the dynamics of metal(oid)s-MPs interactions.

In an aquatic environment, pH and ionic strength significantly influence the process of adsorption/desorption (Tang et al., 2020; Zou et al., 2020), as these parameters determine the reactivity and charge state of polymer surfaces. Overall, the increase of pH solution lead to higher adsorption efficiencies, whereas decrease of pH enhances substantial desorption (Kalčíková et al., 2020; Tang et al., 2020; Lin et al., 2021). At a low water pH, more H^+ ions surround the surface of a polymer, what consequently promotes repulsion of metal cations, resulting in the decrease of adsorption interactions and likely higher desorption from surfaces (Tang et al., 2020). In turn, due to low solubility of metal(oid)s at a basic pH medium (>7), the precipitation of metal(oid)s onto microplastic surfaces is enhanced (Kalčíková et al., 2020; Lin et al., 2021). However, this scenario can be different if anions are involved, as for As ions. Dong et al. (2020) observed decrease of As adsorption onto MPs with increase of pH, reversely to what was acknowledged for cations. Acidic pH promoted adsorption here since observed low concentration of OH^- avoid competition for binding sites with the metalloid anions (Meng et al., 2002; Dong et al., 2020). Furthermore, some polymers (i.e., PS) have a tendency to become negatively charged as the pH increase, resulting in inhibition of the bond with anions through electrostatic repulsion on the surface (Dong et al., 2020), and affinity for cations is enhanced. As matter of fact, positively charge surface attract anions and repulse cations, and vice versa in the case of negatively charged ones. Since water pH establish metal and metalloid ion species, and as bonds with polymer surfaces involve charged sites, the behavior of metal(oid)s towards MPs can be in constant change concerning sorption, over a dynamic pH surroundings. This also supports the main role of electrostatic interaction in the process. Nonetheless, adsorption performance in seawater can fluctuate, as, for the majority of metals, adsorption usually increases under a basic pH (characteristic of seawater) but decreases with high salt content (specific of seawater). In line with this, different behaviors amongst the metal/metalloid ionic forms subject to the chemical properties of the water can be observed. Turner and Holmes (2015) found adsorption of Cd, Co, Ni and Pb to be efficient in freshwater (and high pH), conversely to lower adsorption of Cr, which was found to be higher with respect to seawater (Holmes et al., 2012). Differences concerning water environments suggested that a higher ionic strength promotes complexation and ion pair

with seawater anions and also competition with the divalent seawater cations, decreasing the boding of metal cations (i.e., Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Ag^{2}) and available binding sites on MPs surfaces (Holmes et al., 2012; Turner and Holmes, 2015). The previous example highlights the complexity of the process which needs to consider all intervening variables. Increase of ionic strength entail high levels of sodium (Na^{+}) or potassium (K^{+}) ions what can suppress adsorption of metal(oid)s on surfaces since the presence of more ions encourage competition for adsorption sites with other metal(oid) cations (Holmes et al., 2014; Johansen et al., 2018; Tang et al., 2020). Organic matter also has a role on sorption dynamics, since high concentrations (e.g., fluvic acid) behave as competitor to microplastic particles regarding the uptake of metal(oid)s (Tang et al., 2020). In this way, the higher presence of organic ligands in freshwaters (Santos-Echeandia et al., 2008a) will reduce metal adsorption to MPs that could increase when reaching seawater with a lower ligand content (Santos-Echeandia et al., 2008b). High temperature can also break hydrogen bonds between surface and metal(oid)s, decreasing adsorption (Dong et al., 2020). Additionally, biological activity (e.g., bacterial, worms) potentially foster metal(oid)s removal, as metal and metalloid ions are weakly linked within a biofilm on polymers (Richard et al., 2019). Accordingly, once on environment, MPs can either acquire and/or release associated hazardous substances (i.e., metals and metalloids) enhanced by natural factors and depending on local environmental conditions.

3. Release of metal(oid)s additives from plastics

The presence of metal(oid)s on MPs can also be due to their previous and intended addition. Virgin or recently manufactured plastics already contain chemicals themselves used as catalysts, fillers and plasticizers, applied to keep their properties and resistance (GESAMP, 2015; Castro et al., 2018). Those inherent metal(oid)s can be found in the matrix of polymers and are usually linked by physical and not chemical forces (Turner et al., 2020). Metal(oid)s used as additives in plastics can contribute essentially as fillers, pigments and stabilizers (heat and flame retardants) or they can confer antimicrobial properties (Turner and Filella, 2021). In addition, As is a known toxic metalloid used as a biocide in plastic production. Cadmium, zinc (Zn) and lead are examples of metals commonly used as stabilizers to reinforce the durability of polymers (about 3% composition), and also applied in color pigments of plastics along with Cr and mercury (Hg) (Imhof et al., 2016; Hahladakis et al., 2018; Munier and Bendell, 2018; Town et al., 2018). Highly toxic Hg and Pb are strongly related to production of chlorine groups of PVC polymer (Salvaggio et al., 2019). The exposure to metal(oid)s additives from polymers in the environment is real, as they can be decoupled from the polymer to surrounding water following assimilation on external tissues of organisms (Oliviero et al., 2019) or dissociated inside their bodies to accumulate on internal organs. Turner et al. (2020) suggested the release of desorbed metal(oid)s from the surface of polymers occurring through desorption process. In turn, the element additives are released from the polymer matrix to surrounding water by diffusion (Turner et al., 2020). Regardless, both processes take place in water environments. Even though, in line with predictions of Nakashima et al. (2016), and despite the researchers have quantified the leaching of Pb from marine plastic debris, the hazardous additives of a plastic material are not released in relevant amounts to environment. From the 5100 μg/g of maximum Pb quantified in marine plastic floats, just 0.1% was predicted to be lost to water (Nakashima et al., 2016). In the mentioned study was underlined that is more likely that additive-Pb present at high concentrations in plastic debris is stocked and transported to long-distances than released (leached) from polymers to water during their migration on environment. Accordingly, diffusion of hazardous elements to water occurs at low rates, being potentially no relevant to soon threat ecosystem's health. A reasonable justification for this finding is the fact that the additives were added to the polymer bulk to be an inherent component of the particle itself, being more stable and unlikely to dissociate (Town et al., 2018) unless high degradation of the polymer occurs (e.g., plastic particles washed ashore suffer from more physical degradation over deposition on beaches) (Nakashima et al., 2016). Furthermore, Turner et al. (2020) found high levels of Pb as additive in beached microplastic (PVC, PE, PP) as well, comparing to its presence as adsorbed Pb (PE beached MPs).

Potential transfer of hazardous metals from leaching of plastic toys has been spotlighted as a concern issue to health ware. To minimize the damages associated to the hazardous role of heavy metals, their application in plastic manufacturing became restricted in Europe (Hahladakis et al., 2018). Cd and Pb have been quantified in mostly PVC-based former plastic toys (Miller and Harris, 2015) at levels exceeding the actual EU permissible limits for their production (17 and 23 μg/g, respectively) (Turner, 2018b). This scenario could be worst if plastics are ingested following desorption and accumulation of toxicants in the human body, as ecotoxicological effects have been observed in aquatic organisms (Oliviero et al., 2019) as a result of exposure to plastic toys. Complementarily, no detectable levels for heavy metals were detected in most-recently produced plastic toys (Miller and Harris, 2015), in line with their exclusion in production of these materials. Thus, the high load of heavy metals (e.g., Hg and Pb) used as additives and that have been restricted or banned, is rather found in "old" sampled plastics and reflect the age and residence time of the plastic debris (Filella and Turner, 2018). Apart from the metal(oid)s additives used to strengthen raw plastic material, it is possible to find other sources of their relationship. The industry of electric and electronic equipment (EEE) is a great contributor to plastic pollution, since a large proportion of their resultant waste (WEEE) is composed by plastic, amongst 300 different types (Wäger et al., 2012; Peisino et al., 2019). Although plastic from WEEE is highly potential renewable, it is also composed by metal(oid)s residues (Wäger et al., 2012; Peisino et al., 2019) or reused to make black plastic (Turner, 2018a; Shaw and Turner, 2019), which often end up in aquatic systems. Therefore, the use of Pb, Hg, Cr and Cd as additives with concentrations higher than 1000 mg/L cannot also be applied in the plastic production and recycling of EEE, according to the restriction of hazardous substances (RoHS) directive (Hahladakis et al., 2018). However, until recently, heavy metals were detected in plastic environmental samples exhibiting values above the RoHS directive (Turner, 2018c). Even in recycled plastics as polyethylene terephthalate (PET) bottles, the leaching of hazardous elements was found (Cheng et al., 2010). Despite renewed plastics can have metal(oid)s as a result from reaction of recycled residues, they can also adsorb metal(oid)s once on environment. At last, the transferring of metal(oid)s additives from MPs is causing worldwide preoccupation since they are strongly present in our life with potential consequences.

High color diversity attributed to MPs is frequently associated with different species of metal(oid)s pigments or with different level of degradation of polymers, as mentioned before. Cu can be found in blue and green-colored plastics, while Pb and Cd are also associated to green pigmentation of plastics (Carbery et al., 2020). Reddish-brown plastics are often attributed to Hg and Cd addition. Black and grey colored plastic debris are normally deriving from WEEE, whom contain an expected high metal content (Haarman and Gasser, 2016; Shaw and Turner, 2019). Nonetheless, dark and yellow-colored MPs (e.g., pellets) are also associated to have a high degradation degree promoted by strong weathering, thus with strong capacity to concentrate metal(oid)s from environment. This could explain why colored MPs sampled from environment usually have high metal(oid)s content, as they have higher sorptive capacity and/or high inherent additive content, to further release to environment. In this way, colored MPs, especially the darker ones, can represent a higher risk considering their role as vectors of higher amounts of hazardous substances to aquatic environment. To clarify this and other variables and mechanisms intervening in this process, it is of great relevance to study the polymer-potentially toxic element interactions in controlled laboratory conditions, upon determination of leachable metal(oid)s in plastics with environmental past.

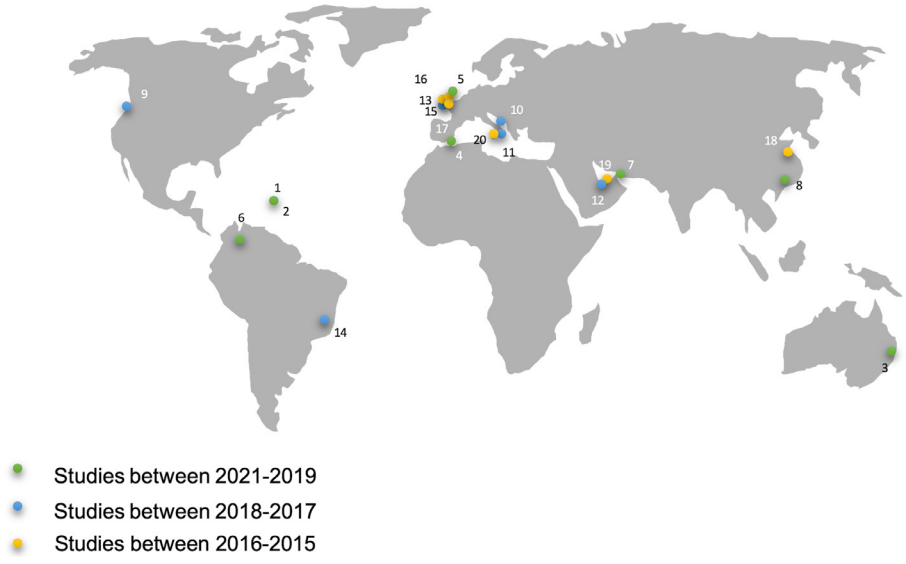

Fig. 2. Field studies all over the world focusing on the determination of metals in plastics from aquatic environments, considering late years (2015–2021). The numbers on the map represent the study and the site where it was performed. (1) Guadeloupe, France (Catrouillet et al., 2021); (2) Guadeloupe, France (El Hadri et al., 2020) (3) Australia (Carbery et al., 2020); (4) Murcia, Spain (Santos-Echeandía et al., 2020); (5) Plymouth, UK (Turner et al., 2020); (6) Cartagena, Colombia (Acosta-coley et al., 2019); (7) Bandar Abbas, Iran (Yazdani Foshtomi et al., 2019); (8) China (Mohsen et al., 2019); (9) Burrard Inlet, Vancouver, Canada (Munier and Bendell, 2018); (10) Croatia (Maršić-Lučić et al., 2018); (11) Lake Geneva, Switzerland (Filella and Turner, 2018); (12) Persian Gulf (Dobaradaran et al., 2018); (13) Whitsand beach, Plymouth (Massos and Turner, 2017); (14) San Paulo, Brazil (Vedolin et al., 2017); (15) Whitsand Bay, Plymouth, UK (Turner and Lau, 2016); (16) Plymouth, UK (Turner, 2016); (17) Plymouth, UK (Turner and Solman, 2016); (18) Beijiang River, China (Wang et al., 2016); (19) Persian Gulf, Iran (Akhbarizadeh et al., 2016); (20) Lake Garda, Italy (Imhof et al., 2016).

Moreover, the colors of the bubbles classify the studies by year range, according to the published year.

4. Studies focused on the metal(oid)s-microplastics interaction in aquatic environments

4.1. Determination of elemental content in environmental plastics

In the last six years, an increasing number of studies have been dedicated to investigate the interactions between plastic and metal(oid)s in the aquatic environment (Turner, 2016, 2018c; Turner and Lau, 2016; Turner and Solman, 2016; Massos and Turner, 2017; Filella and Turner, 2018; Carbery et al., 2020; Turner et al., 2020). Among these studies, large part of them were carried out with plastic material samples collected in the field (Fig. 2) in order to evaluate the environmental behaviors and real contamination concerning MPs and metal(oid)s interactions, while some laboratory experiments explained and reinforce those observations. The regions near Plymouth (UK), mainly beaches as representants of marine environments with high tendency to accumulate plastics, both of land and sea origin, have been commonly chosen as study area in the several reunited studies. In this nearby port region, high amounts of heavy metals (i.e., Pb) were quantified in plastics with total concentrations exceeding the 10,000 μg/g on PE (Turner and Solman, 2016; Massos and Turner, 2017; Turner et al., 2020), polyurethane (PUR) (Turner, 2016; Turner and Lau, 2016), PP and PVC (Turner, 2016; Turner and Solman, 2016; Turner et al., 2020) and lower levels (> 1000 μg/g) also identified on PE and PP samples (Massos and Turner, 2017). Cd was found with maximum concentrations up to 1000 μg/g (Turner and Solman, 2016) on PVC (Filella and Turner, 2018; Turner, 2018c) and Pb even exceeding the 16,000 μg/g on PU (Turner and Lau, 2016; Turner, 2016), plus substantial levels of other heavy metals as cooper (Cu) (> 1000 μg/g) and Cr (> 1000 μg/g) (Turner, 2016). In addition, Zn (> 1000 μg/g on PUR), iron (Fe) (> 1000 μg/g on PE and PUR) (Turner and Lau, 2016), (titanium (Ti) and barium (Ba) (> 10,000 μg/g) (Turner and Solman, 2016) are examples of reported metals in local plastic debris. Metalloids As and antimony (Sb) were also found in environmental plastics but in different orders of magnitude, as 21 μg/g and up to 10,000 μg/g maximum concentrations, respectively (Turner, 2016). In the study of Turner (2016) the presence of Pb was highly associated to prior introduction of lead chromate as additive into plastics, since Cr was tightly quantified together with Pb on the same beach samples. Besides Pb identification in all the beached plastics collected, this potentially toxic element was also estimated as highly bioavailable to local marine birds, according to Turner and Lau (2016) work. Carbery et al. (2020) quantified higher content of metal(oid)s (Mn, Cr, Cu, As, Zn and Pb) in MPs from coastal areas related with industrial regions (e.g., Pb > 8 mg/kg; As > 0.6 mg/kg) comparing to MPs from other associated uses (urban, residential or rural) (e.g., Pb > 1 mg/kg; As > 0.1 mg/kg), evidencing the capacity of MPs to storage (potentially adsorbed) metal(doi)s and transport them over long-distance ranges. Moreover, a color dependency was suggested, as the Cu levels found were likely due to the highest number of blue-colored plastic items sampled there. In this way, as Cu is typically used as metal pigment to confer blue color to polymers, maybe its presence on MPs was more due to its introduction as additives than adsorption from environment. The elemental content found in plastics pieces can reveal the residence time of plastics in environment or demonstrate long-range distances travelled. For instance, all three of the most hazardous elements as Pb (>10,000 μg/g), Cd (>1000 μg/g) and Hg (> 100 μg/g) were found on PVC plastics with levels nowadays restricted, as mentioned in the previous section (Filella and Turner, 2018). Also reported before, was the high amounts of the potential highly toxic Hg being strongly associated to aged darker plastics (blank and reddish-brown) (Acosta-Coley et al., 2019; Santos-Echeandía et al., 2020). Santos-Echeandía et al. (2020) reported initial evidence of the transfer of Hg to biogeochemical cycles through plastics. They quantified Hg (1 to 1600 μg/kg) in all the virgin and sampled beached plastics (mostly PUR and PVC, but also on PE and PP), with higher levels at coastline comparing to upper regions in the beach. Accordingly, additive and adsorbed Hg on MPs flows in ocean, transported until deposition on beaches, where volatilization to atmosphere occur through UV radiation. From this point of view, plastics could remove hazardous elements from water and concentrate them, thus reducing the concentration of dissolved metals on aquatic environments (Santos-Echeandía et al., 2020).

In MPs-metal(oid)s studies, identifying the source of interactions of these pollutants is frequently a struggle that some researchers aim to clear up. Turner et al. (2020) have quantified Pb in marine MPs, which was considerably higher (maximum concentration) as an additive (40,000 μg/g on PVC, PE, PP) than the amounts found to be adsorbed from water (0.1 μg/g on PE). Furthermore, percentage levels of Pb estimated to be released through desorption (i.e., adsorbed Pb) from MPs to a simulated gastric avian solution had a higher proportion (70%) than the levels released from diffusion (i.e., additive Pb) (16%) considering initial concentrations of Pb identified as adsorbed or additive, respectively. However, with respect to absolute concentration of Pb released, the levels were higher (two orders of magnitude) through release of additives. Additives exhibit physical interactions within a polymeric ma-

trix, whereas adsorbed metals link to surface of polymers on active sites forming a chemical bond (Turner et al., 2020). For this reason, reactivity of adsorbed Pb on MPs was higher. Considering that PVC is highly associated with Pb present as additive, perhaps if only the other polymers were used to comparison, as PE which was found not to be an efficient adsorbent of metals (Yu et al., 2019), the disparity between the levels of Pb adsorbed and quantified as additives would not be as significant as was verified in the Turner et al. (2020) work. Another two recent studies were engaged in to develop methods for determination of elements as additives or adsorbed on beached MPs (pellets and fragments) (El Hadri et al., 2020; Catrouillet et al., 2021). El Hadri et al. (2020) identified Cd (< 8 mg/kg) concentrated on PE, and Pb (> 1000 mg/kg), antimony (Sb) (< 25 mg/kg) and Zn (20 mg/kg) on PP as additives. Regardless, Pb and Sb were also found to be adsorbed onto PE, based on generated profiles (qualitative and quantitative criteria) concerning their distribution on MPs subsurface. On the other hand, Catrouillet et al. (2021) applied different release processes to quantify additives (i.e., acid leaching) and bioavailable (i.e., acid total digestion) metal(oid)s from polymers. They found lower metal(oid)s release through leaching (additives) than through digestion (potentially adsorbed elements from environment). However, the authors retained that they method did not estimate additive-sources for leached elements (environmental vs industrial). In this way, more similar comparative studies should be performed resorting to other polymers and metal(oi)s in order to obtain conclusions about differences in the leaching of metal(oid)s added during the manufacturing process or adsorbed once in the environment.

A few researchers compared their results from quantification of hazardous elements in environmental plastics with data of metal contamination in local water (Maršić-Lučić et al., 2018) or sediment (Dobaradaran et al., 2018; Mohsen et al., 2019). Maršić-Lučić et al. (2018) found higher (two orders of magnitude) mean concentration of metals quantified as Cd (2.9 μg/g), Cu (0.21 μg/g) and Ni (0.14 μg/g) in the pellets (unidentified polymers) collected from beach sediment, comparing with their dissolved levels reported on the local seawater (8.5; 338 and 423 ng/L, respectively), and even three orders of magnitude higher on pellets for Pb (0.26 μg/g) and Zn (2.08 μg/g) comparing to their dissolved levels (182 and 722 ng/L, respectively). This results support occurrence of adsorption of metals from the aqueous media to remain on polymers. Mohsen et al. (2019) determined metal(oid)s in MPs accumulated on sediment, and in the sediment itself, from a marine environment in a sea cucumber farm. Among the elements identified, they found higher mean concentration of Cd, Pb, and Zn (0.058–0.99; 2.56–40.8; 16.44–1190 mg/kg, respectively) on the MPs than on the sediment. On the other hand, Dobaradaran et al. (2018) found no significant differences in metal content (i.e., Al, Mn, Cd, Cr, Ni, Pb, Cu) between the two solid phases sampled, except for Fe, which was higher in the sediment (3050 μg/g) than in the MPs (531 μg/g) mean concentration.

As previously indicated, MPs are transported by wind, waves and marine currents and are finally accumulated on the beaches. Once there, the adsorbed metal(oid)s can escape from MPs particles due to the high temperatures reached in the sand of beaches, with respect to the mean temperature of seawater, by means of volatilization. This fact has been already verified for Pb in PE and PE-LD bags (Alam et al., 2018) or Hg volatilized from several types of polymers found on the beach (Santos-Echeandía et al., 2020). Furthermore, chlorine was found to induce volatilization of metals in PVC waste with temperature rise (Osada et al., 2009), namely Pb, Ni and Cu (Yu et al., 2017). This mechanism will act as a source of metal(oid)s accumulated from seawater onto MPs back to the atmosphere and lithosphere. At last, something important to point out in some of the field studies is the lack of polymer identification, in part due to the different binding behavior of metal(oid)s and different polymers. As matter of fact, polymer characterization should be performed in parallel to metal(oid)s determination, since it is an important criteria to scientifically validate studies (Hermsen et al., 2018) and compare the results obtained in laboratory.

4.2. Complementary findings from laboratorial studies

Interaction between MPs and metal(oid)s is complex and has a high variety of variables involved (i.e., polymer type, degradation status, element, presence of organic matter, biogenic coatings, salinity, temperature). The control of this great number of variables in the field is difficult and limits the understanding of the weight that each variable has in the kinetics or potential binding between metal(oid)s and MPs. In order to learn more about this process that could allow to draw up reliable conclusions, several researchers have performed laboratory-controlled experiments testing most part of these variables (Table 1).

Brennecke et al. (2016) observed high adsorption of Cu and Zn onto MPs (virgin PS and aged PVC fragments) previously leached from an antifouling paint to water. PVC obtained the highest adsorption efficiency (850 partition coefficient between polymers and water) with respect to Cu, highlighting the strong adsorption capacity of plastics towards metals and comparing to their dissolved levels on water. Both aged and pristine particles adsorbed the available metals from water, evidencing the reactivity of MPs towards metal ions, even before their properties are modified after environmental exposure. The adsorption capacity of virgin MPs to metal(oid)s was also demonstrated in other studies (Turner and Holmes, 2015; Rivera-Hernández et al., 2019; Dong et al., 2020; Fernández et al., 2020; Mao et al., 2020), although, for the largest part, higher adsorption capacities are attributed to the aged MPs, as reviewed here. Gao et al. (2019) investigated sorption through performance of both laboratory and field tests, considering different times of exposure (9 days and 9 months, respectively) of new commercial plastic particles (PP, PE, PVC, polyamide (PA) and polyoxymethylene (POM)) with different sizes (2–5 mm). Adsorption capacity increased with decrease of particle size and the equilibrium between the heavy metals Pb, Cu and Cd and the MPs was achieved within the 9 days of the laboratorial suspension. The highest adsorbed levels were quantified for Pb, ranging from 0.627 μg/g in PP to 1.318 μg/g in PVC, while the lowest amounts corresponded to Cd (0.002 μg/g) in POM, finding different adsorption trends for the metals tested depending on the polymer type. Considering the field exposure, the highest metal levels (i.e., Pb) were found to be adsorbed on PP (0.109 - 0.144 μg/g) rather than on PVC (0.028–0.107 μg/g), conversely to what was observed from the laboratory experiment. The fluctuation observed in the quantified metals on MPs from the environmental suspension between the two sampling times of 6 and 9 months (first decreased to following increase), suggests a dynamic behavior of metal adsorption onto polymers on nature. That is to say that ions are in constant exchange between the solid and liquid interface, until they reach equilibrium, guided by environmental parameters (Gao et al., 2019). Earlier, Turner and Holmes (2015) performed reaction kinetics between trace metals (Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn) and (beached or new) pellets on a freshwater solution. Pb was identified with a maximum of distribution coefficient in both beached (10^2 mL/g) and virgin pellets (6 mL/g) from water, suggesting about two orders of magnitude higher adsorption capacity for the aged MPs. In turn, the water parameters influence sorption dynamics between metals. Increase of river water pH facilitated adsorption of Ag, Cd, Co, Ni, Pb and Zn, but not for Cr. Surface complexes formed with cations, oxyanions and organic complexes on the natural environment was considered to be the main responsible for the higher reactivity of aged MPs.

A range of several environmental conditions are tested as they influence sorption behaviors between polymer surfaces and metal(oid)s. From a very complete study, Tang et al. (2020) found adsorption of Pb onto nylon MPs increasing with pH rise but decreasing with increase of ionic strength and fulvic acid concentration, representing significant key factors for sorption dynamics. High concentrations of fulvic acid inhibited Pb uptake onto MPs, as this dissolved form of organic matter has more affinity for metals than MPs have, through formation of complexes, and thus, illustrating competition for metal bond. Pb bond was higher with aged MPs and due to electrostatic interaction, with carboxylate groups representing the most important functional group

Table 1
Characterization of experimental studies investigating sorption mechanisms/capacity of MPs towards metal(oid)s and other hazardous elements with influencing variables.

Polymer features	Element	Tested medium	Analytical method	Element initial conc. tested	Time of exposure	Env. factors tested	Ref.
Virgin and beached pellets (PE)	Cd Co Cr Cu Ni Pb	Estuarine conditions	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	0–20 μg/L	24 h	pH	Holmes et al. (2014)
Beached and virgin pellets (PE, PP) Virgin pellets (PE)	Ag Cd Co Cr Cu Hg Ni Pb Zn	Beach	ICP-MS	5 μg/L	168 h	pH	Turner and Holmes (2015)
Aged fragments (PVC) Virgin beads (PS)	Cu Zn	Seawater	Flame Atomic Absorption Spectrometry (FAAS)	–	14 days	–	Brennecke et al. (2016)
Virgin and aged (PE-HD)	Cs Sr	Freshwater Estuary Seawater	X-ray Fluorescence Microscopy	26–35 mg/L	142 days	Biofilms	Johansen et al. (2018)
Virgin pellets (PE, PP, PA, PVC, POM)	Pb Cu Cd	Metallic solutions Seawater	ICP-MS	5 mg/L	11 days 9 months	–	Gao et al. (2019)
Virgin and aged fragments (PET)	Cu Zn	Aqueous solution	ICP-MS	5 mg/L	144–500 h	UV light	Wang et al. (2020)
PVC, PE-LD, PE-HD, CPE	Cu Cd Pb	Metallic solutions	FAAS	0.1–50 mg/L	24 h	pH ionic strength	Zou et al. (2020)
Virgin and aged	Pb	Aqueous solution	FAAS	8 mg/L	48 h	Fulvic acid pH Ionic strength	Tang et al. (2020)
Virgin pellets (PS)	As	As(III) solution	Atomic fluorescence spectroscopy	10–50 mg/L	32 h	pH Ionic strength	Dong et al. (2020)
Aged pellets and virgin films (LD-PE)	Pb	Tap water	ICP-MS	15 μg/L	48 h	UV light	Ahamed et al. (2020)
Virgin and aged (PS)	Pb Cu Cd Ni Zn	Pure water Seawater	FAAS	50 mg/L	48 h	UV light	Mao et al. (2020)
Virgin and aged (PS, PVC)	B	Boric acid solution (dissolved in water)	Inductively Coupled Plasma Emission Spectrometry (ICP-OES)	1 g/L	30 h	Humic acid Ionic strength pH	Wang et al. (2021)
Virgin and aged thermoplastic polyurethane (TPU)	Cu	Deionized Water	FAAS	2.5–50 mg/L	72 h	–	Xue et al. (2021)
Virgin (PE) and pellets (PP)	Cu Cd Pb Zn	Aqueous solution	Atomic Absorption Spectrometry (AAS)	1 mg/L	9 days	pH Salinity	Ahechti et al. (2020)
Virgin (PVC, PE, PS)	Pb	Distilled water	Dithizone method	25 mg/L	24 h	Temperature pH Ionic strength	Lin et al. (2021)

For the characterization of the studies, were considered the following parameters: Polymers features, Element, Tested medium, Analytical method to quantification of elements (Analytical method), Elemental initial concentration tested (Element initial conc. tested), Time of exposure, Environmental factors tested (Env. Factors tested), and reference (Ref.).

in this process, along with surface complexation (Tang et al., 2020). Surface complexation and electrostatic interactions were reported for many studies to be the main responsible to bond metal(oid)s (e.g., Pb, B, Cd, Cu) to polymer surfaces (Tang et al., 2020; Zou et al., 2020; Wang et al., 2021). Zou et al. (2020) confirmed the mentioned mechanisms as main responsible for sorption of Cd and Cu, but stronger electrostatic interaction for Pb, on commercial polymers. Here, higher adsorption of heavy metals on the chlorinated polymers tested CPE and PVC was identified (adsorption capacities followed CPE > PVC > PE-HD > PE-LD) with higher adsorption efficiency for Pb, followed by Cu and finally Cd (Zou et al., 2020). Electronegativity of CPE polymer dictated its strong bond with cations. Also, the oxidation of PE-HD with formation of CeO/C=O groups allowed higher adsorption for this polymer, in relation to PE-LD. Despite high pH allowed strong adsorption, ionic strength had not a significant influence on the process, conversely to the findings from other studies. In turn, adsorption of Pb demonstrating the influence of different salinities and depending on polymer type of MPs was reported by Lin et al. (2021). Here, the maximum adsorption amount for Pb between polymers was as follows: PE (531/459 μg/g), PVC (476.9/328 μg/g) and PS (246.4/227.1 μg/g), respectively for lower and higher ionic strength. Holmes et al. (2014) early related high salinity with decrease of adsorption capacity towards metals (i.e., Pb) promoted by the competition between cations for available surfaces to settle from water. Furthermore, the effect of ageing mechanism on MPs concerning sorption has been investigated by Mao et al. (2020) and Wang et al. (2020). Mao et al. (2020) induced photo-aging on PS and their sorption behavior towards a few metals (Pb, Cu, Cd, Ni, Zn), while Wang et al. (2020) tested influence of UV light on PET and their affinity for Cu and Zn. From both studies was possible to acknowledge that exposure to UV irradiation is a determinant factor enhancing the sorption capacity of wasted plastics towards metals on environment. After UV induced-aging, an increase of cracking, pore size, roughness, and creation of new oxygen-containing functional groups to reaction with metals on water was observed. This consists in the major alterations on the polymer surface as photolysis enable the break of chemical bounds (e.g., C-H), which originate new functional groups by reaction with free radicals with oxygen, thus forming C-O and C=O bounds. Additionally, the influence of external factors was also explored by Wang et al. (2020) in the same study, who found enhancement of adsorption of metals onto surfaces when exposed to high temperature (with maximum sorption capacity of 268.4 μg/g for Cu at 318 K) and high pH (Cu achieved 282.5 μg/g on MPs at pH 7).

Additionally, Richard et al. (2019) identified biofilm (adhered to plastic surfaces after exposure in estuarine waters) as the most signif-

icant variable promoting uptake of metals on polylactic acid (PLA) and low-density polyethylene (PE-LD) new pellets. Biofilm coverage was identified on the same polymer (PE-LD) for Ahamed et al. (2020), subject to potable water plumbing pipes, to strongly facilitate adsorption of Pb (1602 $\mu g/m^2$) comparing to their absence (124 $\mu g/m^2$). In terms of sorption equilibrium, Pb onto MPs with no biofilm was achieved over 6 h while the 5 days of exposure for biofilm-covered MPs were not enough to achieve equilibrium. This observation could reflect the more available sites for metal(oid)s created by complexes with biofilms on MPs surface. Furthermore, microbial communities contain natural polymers which have functional groups with negative charges (e.g., OH^-, SO_4^{2-}) likely favoring the bond with metal cations (i.e., Pb^{2+}). The competition of Pb^{2+} with other cations for limited available active sites and the ion pair with anions (forming more soluble complexes) decreases its activity towards polymers (Ahamed et al., 2020). Accordingly, the presence of chlorine residuals on water (characteristic of tap water tested as background solution here) delayed the equilibrium achievement of Pb onto pellets (135 $\mu g/m^2$ and 95 $\mu g/m^2$ in their absence and presence, respectively). Formation of chloro-complexes with Pb and oxidation to precipitation of Pb ions is suggested to inhibited metals-MPs adsorption. Overall, the uptake of metal(oid)s essentially occurs on freshwater environments (biofilm growth) to be further transported until marine environments to be potentially released there.

Among the revised studies, a higher affinity of polymers for Pb is evident, as its cations have a strong electronegative interaction with polymers allowing their bond (Zou et al., 2020). The high toxicity and high potential bioaccumulation, adding up their wide use as plastic additive makes Pb (Lavers and Bond, 2016a; Nakashima et al., 2016; Tang et al., 2020; Turner et al., 2020) and also Cu (Holmes et al., 2014; Turner and Holmes, 2015; Brennecke et al., 2016; Gao et al., 2019; Xue et al., 2021) as the main elements used as metal models in field and laboratory studies. Additionally, Pb was demonstrated to be highly adsorbed onto polymers, especially PVC (Brennecke et al., 2016; Gao et al., 2019; Tang et al., 2020; Zou et al., 2020), and with a high desorption potential (Turner et al., 2020). The high adsorption capacity of PVC is common for several studies, especially for Cu, Pb and Cd, which is attributed to its higher surface and polarity (Brennecke et al., 2016; Nakashima et al., 2016; Filella and Turner, 2018; Munier and Bendell, 2018; Gao et al., 2019; Santos-Echeandía et al., 2020). Wang et al. (2021) supported high adsorption of PVC towards boron (B) metalloid compared to PS polymer, which were as follows: aged PVC (0.91 mg/g) > aged PS (0.197 mg/g) > virgin PVC (0.1 mg/g) > virgin PS (0.005 mg/g). Accordingly, aged was an enhancer of adsorption through the link of $B(OH)_3$ species with functional groups with oxygen formed, while PVC stand out likely due to C/Cl bond with B. Moreover, from other parameters tested, the presence of humic acid and high pH restrained the bond of B to MPs. Although, polymer type, ion type (represented here by Mg^{2+}, Ca^{2+}, Cu^{2+}, and Al^{3+}) and ion concentration were defined as main drivers in sorption process of boron. As an example, at pH 7 (with domain of B(OH)3 species), adsorption of polymers (aged and virgin PVC, aged PS) decreased under low concentration of Ca^{2+} (0.04 – 0.4 g/L), suggesting competition of other cations with B(OH)3. However, cations can also behave as bridges for boron ($[B(OH)4]^-$ species) for negatively charged MPs, as PS. Despite increasing of ionic strength (with more Na^+) enhanced adsorption of B onto aged PVC, inhibition caused by ion competition (i.e., Mg^{2+}, Ca^{2+}) suggests annulation of salinity effect. At last, desorption of previously adsorbed B onto aged PVC under a simulating digestive solution of warm-blooded animals resulted in high desorption rates (35.9%). Another study with a metalloid (i.e., As) was performed in order to understand the mechanisms towards sorption of MPs (Dong et al., 2020). Lower sizes of particles (higher surface area) and lower temperatures increased adsorption. As matter of fact, with temperature increase, hydrogen principal bounds between As(III) and carboxyl functional groups of PS were broken. Moreover, pH rise and also NO_3 and PO_4^{3-} also inhibited adsorption (resulted from competition of arsenate ions with OH^-), supporting the role of electrostatic interaction occurring between As and PS particles here (exhibiting a positive electrostatic potential on surface). Despite the tests conducted in laboratory considering one or a few metal(oid)s to test, on a real aquatic environment it is needed to take in account competition with other ions for binding sites, thus behaviors can be countered there.

From the several types of plastics tested, pellets are the main representatives of primary MPs used in both field and laboratory studies assembled here (Turner and Holmes, 2015; Vedolin et al., 2017; Maršić-Lučić et al., 2018; Richard et al., 2019; Holmes et al., 2020). In environmental studies, these MPs are chosen to be good targets of biofouling and proper indicators of environmental pollution from their quick spread. The findings of studies confirmed pellets as efficient adsorbents of metal(oid)s, with potential repercussion to further transport them from their original source to long distances to be available to a high diversity if organisms.

5. Ecological repercussions from interaction between microplastics and metal(oid)s

5.1. Role of microplastics on the bioavailability of metal(oid)s

Aquatic organisms are daily exposed to a high diversity of plastic debris in their environment from nano- to micro- and macro- plastics. Because of their small size, MPs can easily enter the bodies of organisms either by direct ingestion or through filtration on epithelial organs, following accumulation on their tissues (Wang et al., 2018). The high surface-volume ratio of MPs enables the formation of several bonds with different elements present in the surrounding water. This fact makes these microparticles being responsible for the transfer of a potentially toxic mix of metal(oid)s (adsorbed or as additives) to the circulatory systems of aquatic biota. The acidified environment in the gut of an organism is what promotes the undirect assimilation of chemicals, since desorption and release of metal(oid)s from polymers can be much higher in acidic conditions (30 times faster) than in fresh and seawater (Bakir et al., 2014; Holmes et al., 2020; Tang et al., 2020). Later, after assimilation and upon bioaccumulation, metal(oid)s can turn back to the aqueous media through faeces (Rivera-Hernández et al., 2019) or metabolic mechanisms to elimination of the toxicants in a more soluble and available form to be adsorbed again (Fig. 3). The retention time of MPs in the stomach and digestive tract of aquatic animals (e.g., fishes, bivalves) normally reflect short-time periods (hours to a few days). Although, this time is enough to allow desorption of metal(oid)s from MPs and uptake on tissues. Subsequently, organisms tend to excrete the microparticles, as they have no nutritional content (Gonçalves et al., 2019). In this case, if the bond of metal(oid)s to the MPs is strong, the microparticles can reduce or prevent potential effects from metal(oid)s in contact with organisms, even if they are ingested. In this way, MPs can be vectors of chemicals to aquatic species in two ways (Rodrigues et al., 2019), since the contact with these particles can contribute to increase or reduction on the assimilation of coexisting hazardous elements and toxicological effects (Khan et al., 2015; Lu et al., 2018; Rivera-Hernández et al., 2019; Rodrigues et al., 2019).

5.2. Bioaccumulation, ecotoxicity and reported scenario effects

It is relevant to estimate the potential of MPs-associate metal(oid)s to be desorbed upon (or before) ingestion by aquatic organisms and subsequent effects (i.e., bioaccumulation and toxicity). Studies reporting the impact of MPs on aquatic organisms are extensive. Yet, a few years ago, just a few of them focus on toxicity concerning exposure to metals associated to MPs (de Sá et al., 2018). Characterization of several bioassays with single, coexposure and exposure to MPs and (preadsorbed) metal(oid)s with reported effects derived from their interaction are presented in the Table 2. Khan et al. (2015) tested the influence of MPs in the uptake and path-route of silver (Ag) on *Danio rerio*. The treatments with MPs differed between (1) exposure to previously bounded Ag to

Table 2
Experimental studies of impact of microplastics on bioaccumulation and toxicity effects of metals on aquatic organisms resulted from the simultaneous exposure of microplastics and metals.

Exp.	Elem. conc. (µg/L)	MPs conc. (mg/L)	Organism	Bioac. of metals by MPs	Analytical method	Effects	Time exp.	Ref.
Ag bounded to MPs and coexposure of Ag and MPs	1 (ER)	10–1000 (PE)	*Danio rerio*	No (Decrease of Ag)	Radiotracer	No effect from co-exposure Decrease of Ag accumulation (Ag-bounded MP)	24 h	Khan et al. (2015)
Coexposure of Cr and MPs	5600–28,400 (NER)	10–1000	*Pomatoschistus microps*	–	–	Oxidative damage Neurotoxicity Decrease of predatory performance MPs suppressed mortality from Cr	96 h	Luís et al. (2015)
Ni and MP mixture (bonded and dissociated)	1000–5000 (NER)	1–30 (PS, PS-COOH)	*Daphnia magna*	Yes	ICP-MS	Immobilization from MPs copresence (higher with PS-COOH) Higher accumulation of Ni through MPs	48 h	Kim et al. (2017)
Cd combined with MPs	10 (ER)	0.02–0.2 (PS)	*Danio rerio*	Yes	ICP-MS	MPs increased Cd toxicity Oxidative damage and inflammation	3 weeks	Lu et al. (2018)
Hg and MPs mixture	30 (ER)	0.13	*Corbicula fluminea*	No (decrease of Hg)	Silicon UV diode detector in an automatic Mercury analyzer	Antagonism in FR, ChE activity, GST activity and LPO levels	14 days	Oliveira et al. (2018)
Hg and MPs mixture	10 – 16 (ER)	0.26- 0.69	*Dicentrarchus labrax*	Yes	AAS with silicon UV diode detector	Oxidative damage	96 h	Barboza et al. (2018)
Cu Cd Pb alone and MPs alone	10 - 50 (ER)	0.33 (PE-HD)	*Hippocampus kuda*	No	ICP-MS	Growth reduction	45 days	Jinhui et al. (2019)
Cu and MPs mixture	10 (ER)	0.02 (PE)	*Prochilodus lineatus*	No	AAS	Genotoxicity Neurotoxicity Physiological effects	24–96 h	Roda et al. (2020)
Ag bounded to MPs	10,000 (NER)	10–100 (PE)	*Lemna minor Daphnia magna*	–	–	Decrease of specific growth Immobility	48 h	Kalčíková et al. (2020)
Hg bounded to MPs	2.5 (ER)	2 (PE-HD)	*Mytillus galloprovincialis*	Yes	ICP-MS	Higher accumulation of Hg on gut from MPs Faster elimination of Hg by MPs	7 days	Rivera-Hernández et al. (2019)
Cu and MPs mixture	500 (NER)	10 (PVC)	*Chlorella vulgaris*	–	–	Growth inhibition (at low MPs conc. single exposure but not at high levels of MPs) Growth increase from coexposure of MPs and Cu	10 days	Fu et al. (2019)
Pb bounded toMPs	1500–2500 (NER)	5–20 (PS-COOH)	*Ceriodaphnia dubia*	Yes	Graphite furnace atomic absorbence spectrometry (GFAA)	MPs enhanced Pb toxicity and accumulation Algae reduced toxicity of MPs-Pb Accumulation of MPs and fast elimination	24 h and 7 days	Liu and Wang (2020)
Cu and MPs coexposure	15 – 125 (ER)	2	*Danio rerio* (larvae)	–	–	Neurotoxicity Avoidance behavior disruption Oxidative stress Antagonism	96 h	Santos et al. (2020)
Cu and MPs coexposure	60-125 (ER)	2	*Danio rerio* (larvae)	Yes	Electrothermal atomic absorption spectrometry	Synergism Neurotoxicity Oxidative stress Mortality	14 days	Santos et al. (2021a)
Cu and MPs coexposure	60-125 (ER)	2	*Danio rerio* (larvae)	Yes	Electrothermal atomic absorption spectrometry	Neurotoxicity Avoidance behavior Mortality	14 days	Santos et al. (2021b)
Cu-MPs and Cd-MPs co exposure	1000-2 000 (NER)	100 (PS)	*Triticum aestivum*	No (decrease of Cd and Cd)	AAS	MPs promote decrease of toxic effects	2 days	Zong et al. (2021)

For the characterization of the studies, were considered the following parameters: Exposure way (Exp.), Elemental concentration tested (Elem. conc.), Microplastics polymer (MPs polymer), Microplastics concentration tested and polymer (MPs conc.), Tested organism (Organism), Bioaccumulation of metals through MPs (Bioac. of metals by MPs), Analytical method, Effects, Time of exposure (Time exp.), and Reference (Ref.). ER identifies Environmentally Relevant tested concentrations and NER correspond to Non-Environmentally Relevant tested concentrations.

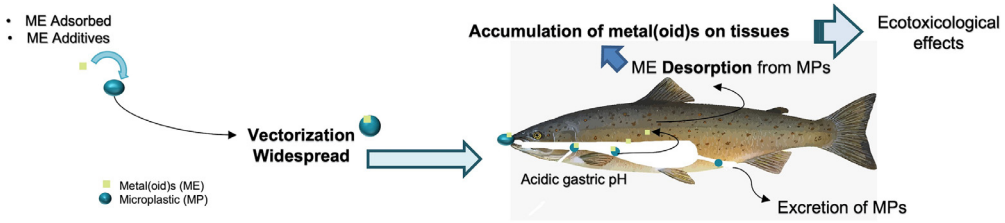

Fig. 3. Process of vectorization of metal(oid)s through microplastics resulted from exposure of aquatic organisms to those related pollutants that result in an ecological impact.

MPs and (2) coexposure of Ag and MPs initially dissociated in the aqueous solution. Exposure of bonded Ag to MPs resulted in the reduction of metal uptake by the organisms, comparing with the levels accumulated from Ag alone, and different accumulation between the organs of the fish, which was higher in their gut. However, the mixture of MPs and Ag (dissociated) had no influence in the bioaccumulation and localization of Ag. These observations demonstrate that the differences in the way of exposure of organisms to chemicals can result in different observations (as they are previously bounded before exposure or not), concerning the bioaccumulation of metals through MPs and potential toxic effects. According to the findings of Rivera-Hernández et al. (2019), Hg ingested via its association with MPs did not affect substantially the levels of Hg accumulated in *Mytilus galloprovincialis* in comparison to the Hg associated to microalgae or to dissolved Hg. The tested mussels ingested the microparticles to further excrete them through faeces over the depuration time and even the Hg levels in their bodies was higher via water than through MPs (Rivera-Hernández et al., 2019). Additionally, the levels and target tissues for this metal were different between microparticles (microalgae and MPs) and via water, with higher Hg accumulation via MPs or microalgae in the digestive gland whereas via water higher levels of Hg were quantified in gills. Accumulation of Hg is readily facilitated through Hg-microalgae than for MPs, since dissociation of Hg from microalgae is easier to followed absorption on tissues, despite they allowed similar Hg accumulation on organisms, as consolidated by Fernández et al. (2020). These observations suggest that ingestion through MPs facilitates elimination of an hazardous element due to the strong bond of Hg to polymers (Rivera-Hernández et al., 2019). These studies provide evidence towards the role of MPs on the bioavailability of metal(oid)s, even tough, they promoted the reduction on the assimilation of associated hazardous elements and potentially preventing toxicity effects, pointing to a positive action of MPs concerning other toxicants. Bioaccumulation of Hg was also verified to be reduced in the presence of MPs on the clam *Corbicula fluminea* (Oliveira et al., 2018), compared to the heavy metal exposed alone. Ecotoxicological effects were estimated here, with observation of antagonism between the two pollutants in the coexposure of Hg and MPs, since the effects were minimized in relation to their single exposure effects and highlighting existence of interaction and prevention of potential toxic effects from Hg to clams. However, exposure to MPs alone induced neurotoxicity on the organisms. Besides these results support MPs as favorable to prevention of toxicity from the associated metal, MPs themselves are toxic to organisms, perhaps due to inherent metal(oid)s additives they have. One thing in common in the previous cited studies (Oliveira et al., 2018; Rivera-Hernández et al., 2019) is that the tested organisms are bivalves so they easily ingest (or filter) the MPs as they represent particle filter-feeding organisms so they have efficient strategies/mechanisms associated to their digestive system to elimination of non-nutritive particles (and associated toxicants). This could be an advantage over other classes of organisms, dictating different results of bioaccumulation and toxic damage from exposure to metal(oid)s via MPs. For instance, Barboza et al. (2018) reported high toxicity in fish (*Dicentrarchus labrax*) from the exposure to MPs with Hg, as neurotoxicity, oxidative stress and damage. Besides the interference of MPs in the levels of bioavailable Hg, the single exposure of MPs also induced high toxicity on organisms. Luís et al. (2015) estimated toxicity effects on fish juveniles (*Pomatoschistus microps*), as neurotoxicity with inhibition of Acetylcholinesterase (AchE) enzyme activity and decline of predatory performance, inflicted by coexposure to MPs and Cr; and also by MPs alone. However, single exposure of Cr caused mortality, which points to MPs suppressing mortality of the organisms here. Jinhui et al. (2019) observed low body growth and decrease on survival of *Hippocampus kuda* exposed to MPs carrying Cu, Cd and Pb. Despite bioaccumulation of the heavy metals was observed in the sea horses, it was not determined to be as a consequence of MPs vectorization. This work suggested that the toxicity inflicted is more due to the metals than to the MPs themselves. In line with the previous study, Roda et al. (2020) did not observe a vector effect from MPs in the levels of Cu absorbed on *Prochilodus lineatus* tissues, although, genotoxicity in fishes was identified, but with no aggravation caused by the interference of MPs. Conversely to the previous findings (Jinhui et al., 2019; Roda et al., 2020), MPs prompted bioaccumulation and toxicity of Cd, such as oxidative damage and inflammation on *Danio rerio* (adult fish), resulted from the long-term coexposure of Cd and MPs (Lu et al., 2018). Other studies with *Danio rerio* were conducted in order to investigate effects from co-exposure of MPs and Cu in fish early life stages were conducted (Santos et al., 2020; Santos et al., 2021b, 2021a). In these studies, toxicity (neurotoxicity, oxidative damage, avoidance behavior disruption) and even mortality (Santos et al., 2021a, 2021b) for all the single and mixture exposures were reported. Neurotoxicity is a commonly reported toxicity effect on fish resulting from coexposure to MPs and several metals (Luís et al., 2015; Oliveira et al., 2018; Roda et al., 2020; Santos et al., 2020, 2021b, 2021a). Even so, antagonism over 96 h (Santos et al., 2020) or synergism after 14 days (Santos et al., 2021a) were observed between Cu and MPs, regarding biomarkers response, reflecting the relevant impact of MPs over toxicity. Moreover, bioaccumulation of Cu through MPs was observed after 10 and 14 days of exposure (Santos et al., 2021a). Those findings also highlight the influence of the time of exposure concerning the impacts of MPs on toxicity of hazardous substances.

Environmental or environmentally dependent characteristics (e.g., food content, residence time and degradation status of particles, exposure time) are important to influence response of organisms towards exposure of MPs and associated chemicals. One would expect that a long-term exposure of metal(oid)s through MPs cause higher bioaccumulation and toxic damage to organisms than acute toxicity from a brief exposure (Lu et al., 2018). Since metal(oid)s globally exist in trace concentrations in the marine environments, the amounts potentially transferred there in a short period of time could not be high enough to cause immediate effects or accumulation. Even so, a long-term contact with contaminated MPs, as they are ubiquitous and potential sink of metal(oid)s, can magnify the bioaccumulation of toxicants through gradual uptake (Brennecke et al., 2016). The modifications that MPs went through on environment (e.g., formation of new functional groups, biofouling) conferring them a higher frequency bond with metal(oid)s obtained from water, potentially represent higher risk for aquatic biota or preventing them to suffer from toxicity effects, due to the strong bond between the pollutants. Kalčíková et al. (2020) observed higher toxicity on *Daphnia magna* and *Lemna minor* exposed to virgin MPs and also simulated aged MPs containing biofilms both with adsorbed silver than the toxicity observed from pristine and aged MPs alone. Virgin MPs and aged MPs both with adsorbed Ag induced decrease of specific growth rates

(at the highest concentration of MPs) on *L. minor* and immobility on *D. magna*, compared to their single exposure without Ag. However, no difference in the magnitude of toxicity between aged and pristine MPs (with Ag) was demonstrated. Moreover, biofilm was found to also contribute to higher sorption capacity to MPs carrying metal(oid)s, since MPs with a biofilm adsorbed about 44% more Ag than pristine ones, and with higher released amounts of Ag as well, concerning desorption to an acidic medium. Kim et al. (2017) exposed *Daphnia magna* to Ni and MPs (PS and PS-COOH) and observed synergistic effects and bioaccumulation increase from their mixture. Immobilization of the crustaceans was higher through PS-COOH, however, the functional group or lack of it did not influence on the bioaccumulation level of Ni. It is important to say that, despite bioaccumulation overall increased in a dose-dependence perspective over the mixture treatments, it was observed a reversal concerning the highest tested concentration of Ni (5 mg/L). This finding is important to highlight the importance of chemical tested concentrations, as the results can change considering different circumstances. Liu and Wang (2020) introduced algae to test the influence of a natural food pathway on the impact of MPs to Pb accumulation and toxicity on *Ceriodaphnia dubia.* Bioaccumulation and toxicity of Pb to the crustaceans was higher when the metal was bond to MPs, compared with their single exposure. However, in the presence of algae, the Pb toxicity caused through MP significantly decreased. It's important to retain that the algae also allowed assimilation of Pb, but reduced toxicity. Synergism with aggravation of the effects from coexposure of polymers and metal(oid)s, compared with their single exposure, being size- and dose-dependent was demonstrated in a study with nanoplastics (Lee et al., 2019). Bioaccumulation and induced inflammatory responses on *Danio rerio* from nano PS and gold (Au) exposure were higher considering the lowest size of nanoplastics (50 μm) with accumulation in the whole body through the penetration of membranes and particularly accumulation in the lipidic areas. The smaller the plastic particles (i.e., microplastic and nanoplastics) enter inside organisms, the richer in hazardous elements they will be exposed and bioaccumulate.

At last, a few studies investigated the impact of leaching additives from MPs (or adsorbed afterwards) to different classes of aquatic organisms. Oliviero et al. (2019) exposed marine planktonic organisms (*Paracentrotus lividus*) to commercial plastic material toys (micronized PVC at 0.3–30 mg/L) and also to their hazardous elemental additives (mainly Zn with maximum concentration of 1446.1 μg/L) previously leached to water. A decline and delay of urchin embryo and larvae development, and even its blockage (from the highest concentration), was observed from the MPs exposure. From the released hazardous substances exposure, an early delay on development and deformities was also reported. These results evidence the toxicity on organisms caused by MPs and their metal(oid)s components. Furthermore, the researchers also detected a color dependence for the toxicity observed, mainly explained by the different mix metallic pigments added to confer it. Despite the toxicity observed from microplastic leachates, no toxicity was observed when the organisms were exposed directly to PVC virgin ones or to their leachates (tested as control). In other respect, Karami et al. (2017) used low concentrations of MPs (LDPE) fragments (5, 50 and 500 μg/L) in their bioassay with *Danio rerio* to investigate the toxicity effects of potentially leached pollutants (concentration of heavy metals and other chemicals were below the LOD) and find that environmental realistic concentrations of MPs just cause minimal ecological impact. Nobre et al. (2015) obtained higher toxicity in sea urchins (*Lytechinus variegatus)* exposed to virgin MPs (PE) than from those beach sampled, suggesting higher toxicity attributed to hazardous additives than those adsorbed on environment. Although, they did not determine or quantify the substances present on the polymers. Nonetheless, those findings point to leachate metal(oid)s additives from virgin MPs being more hazardous to aquatic species, as they are typically associated to high concentrations of heavy metals, especially the old-produced ones. These findings are in accordance with the study of Turner et al. (2020) who used simulated gastric conditions of seabirds to estimate bioaccessibile Pb from MPs, referred in a previous topic. Here, the adsorbed metal was more biaccessible (70% of the quantified adsorbed Pb versus 16% of quantified additive Pb). However, metal additive content released was much higher (two orders of magnitude) due to higher content quantified on the MPs, so it was considered to represent a higher ecological risk (Turner et al., 2020). Despite metal(oid)s adsorbed from the environment are more easily desorbed to water from polymers, the metal(oid)s added during manufacturing have a higher impact to aquatic biota and ecosystems. This is justified if ingested by organisms, as MPs and metal(oid)s are dissociated in acid conditions (i.e., gastrointestinal tract) in a larger scale to follow assimilation of toxicants in biological tissues. Other studies used the previous referred method with adaptations to estimation of the bioaccessible levels of hazardous elements (additive or adsorbed) released from MPs to digestion solutions. Avian physiologically-based extraction test (PBET) (Turner, 2018c; Holmes et al., 2020) or dietary-adapted with fish oil (DA-PBET) (Smith and Turner, 2020) were applied to the method. All the quantified elements (i.e., Pb, Br, Cd, Cr, Co, Fe, Mn, Se, Ba, Sb, Hg) tested were bioaccessible, among the different studies. Although, Pb, known as one of the most toxic metals, was found to be totally bioaccessible (100%), with maximum release from beached polyurethane exposed to the DA-PBET (Smith and Turner, 2020), and also high levels bioaccessible (80%) from beached PE (Holmes et al., 2020) to PBET. Although, bioaccessible levels for Cd were found to substantially vary (65%) from consumer polycarbonate-acrylonitrile (Smith and Turner, 2020) to less than 1% from PE and PP marine MPs (Turner, 2018c) through PBET digestion. This fact demonstrates that the release and bioavailability of elements from MPs vary and is dependent on nature and source of polymers, type of additive/residue, extraction solution and model. Therefore, high levels of metal(oid)s can be released in high amount from both pristine and weathered MPs.

Susceptibility of seabirds on their own environment to exposure to either adsorbed or inherent metals through local plastic debris has been investigated. Lavers et al. (2014) related the trace elements amounts found in the feathers of seabirds (*Puffinus carneipes)* with the ones determined in sampled plastics. The high levels of Cr found were likely associated to the plastic load, as this metal is known as an additive for the main polymers found inside the organisms and likely responsible for the observed reduction of body condition, caused by vectorization through MPs. These observations support plastics as responsible for transferring of hazardous elements on environment and demonstrate that aquatic organisms (e.g., seabirds, bivalves) can monitor the local load of metal(oid)s not just accumulating them from water (in their dissolved form), but also through MPs ingestion; such as the MPs themselves.

One of the factors or plastic properties that was mentioned here to potentially have an influence on metal type or concentration is the color. Additionally, color of polymers can influence the uptake of MPs by organisms, as they ingest selectively a plastic piece by color for resemblance with the natural color of their prey (Lavers and Bond, 2016b). Consequently, polymer color can determine the assimilated elements (due to leaching of remaining pigments) on their bodies with corresponding toxicities. Since MPs are easily mistaken by any prey and are present in endless numbers on aquatic environments and numerous colors (especially pellets used to make plastic products), the potential impact by metal(oid) additives/adsorbed transferring is worrying.

Regarding plastic size, MPs represent higher risk to aquatic organisms than larger plastics, as well as they can reach almost all levels of the trophic chain, from planktonic organisms (Kalčíková et al., 2020) through bivalves (Rivera-Hernández et al., 2019), fishes (Khan et al., 2015; Luís et al., 2015; Lu et al., 2018) and birds (Weitzel et al., 2021) up to cetaceans (Moore et al., 2020), directly by ingestion/filtration or through bioaccumulation on their bodies (Wang et al., 2018). One would expect nanoplastics being even more alarming than other sized plastics, as they have an even larger surface area, which is directly proportional to a higher sorptive capacity, inducing higher reactivity to

metal(oid)s species (van Leeuwen et al., 2013; Town et al., 2018). Furthermore, nanoplastic particles are so small that can go through chorion membranes (by penetration of the pores) of early life stages of fish (i.e., zebrafish) just by their contact on water to further achievement of all organs to accumulation and undergo potential toxicity of related hazardous elements (Lee et al., 2019). Thus, plastic particles have a size-dependent accumulation pattern on organisms, exemplified here by the chorion holes acting as a barrier to the entry of foreign larger particles, which is also correlated to the extent of induced accumulation/toxicity of associated toxicants on body organisms. It is not clarified whether organisms are or not selective in relation to polymer type regarding MPs uptake (Digka et al., 2018; Town et al., 2018). However, as charged chemical species can be related to a specific polymer type available to bind, regarding its structure and functional groups, a microparticle of a specific polymer ingested could dictate the potential toxicological effects inflicted on an organism.

It is worth to say that the majority of the studies mentioned employed pristine MPs, instead of expose organisms to aged ones. However, aquatic biota are much more likely to be exposed to environmental and degraded plastics, with higher sorptive capacity to concentrate metal(oid)s, reducing bioavailability (Nobre et al., 2015), or enhancing it through transference of the metal(oid)s upon ingestion of MPs by the organisms. Furthermore, benthic and demersal organisms are presumably more exposed to high density polymers, such as PVC (non-buoyant), whereas pelagic ones should be more exposed to low density ones, just as PE and PP, that also correspond to the most produced and wasted plastics. PE was the most tested polymer with respect to bioassays, thus, desorption studies to estimate the potential effects of associated metals should be conducted in the rest of existing polymers, mainly in the most produced ones like PP, PS or PVC, and according to their susceptibility to each polymer in order to guarantee the environmentally reliability of the study. Nonetheless, low density MPs can be scavenged from the water column and reach the sediments following the incorporation of silt and clay materials or biofilms, as described on previous sections.

Which is common for the most part of the studies reported here is that MPs alter the bioavailability of associated metal(oid)s with inflicted toxic effects on organisms just by themselves which are aggravated or not by their association to metal(oid)s. Micronized size allows ingestion of plastics for the majority of organisms (independent feeding stages), making MPs more dangerous than larger ones. At last, concentration of MPs can manipulate impact results.

6. Contribution and challenges of laboratory studies to ecological risk assessment

To date, literature has been inconsistent in respect to estimation of ecotoxicological impact caused by MPs and associated contaminants spread on aquatic environments (Rodrigues et al., 2019). Field studies are more representative of what is factually occurring on nature, although exposure effect and all variables involved are difficult to manage (Anbumani and Kakkar, 2018). Apart from this, availability of controlled experimental studies investigating dynamics and effects is massive and reveals some heterogeneity on methodologies. Hermsen et al. (2018) reunited ten essential criteria to quality assessment of ecological studies focused on uptake of MPs by marine biota. Among them, it is highlighted the sample size, negative and positive controls, target component and polymer identification. Provide all this information on a scientific paper is mandatory in order to assure reliability and reproducibility of a study and enable comparison between obtained findings and other similar studies. The researchers have also classified quantitatively field studies on the subject and obtained an average of negative results regarding accumulative reliability scores (as they failed in at least one criterion), highlighting the lack of standardized methodology. As matter of fact, one key element often revealing the discrepancy between studies is the concentrations used of both MPs and chemicals in test. Reports of Scientific Advice Mechanisms (SAM, 2019) and Scientific Advice for Policy by European Academies (SAPEA, 2019) are specially critical with the concentrations used in laboratory works. Reliable concentrations should be the main element to take into consideration when a study is focused in the real impact of MPs to environmental toxicology, as evaluation of ecosystem's health represents the scientific relevance prompted to perform such work. However, it is possible to observe a mismatch on the tested concentrations and environmental realistic ones on published data, caused by the existence of a gap between theoretical methods to estimate the number of plastics and their impact on food web transfer SAPEA (2019). For instance, concentrations of pollutants in sea and open ocean are lower than in coastal areas which should be considered when designing the experiments. Since impact of MPs, considering their relation to contaminants, is a novel research field, the focus to soon publish data frequently overlaps the optimization of reliable methodologies. Nevertheless, some studies concern in to use environmental or low concentrations to obtain reliable answers on toxicity of MPs and associated contaminants (i.e., metal(oid)s) to aquatic biota (Jinhui et al., 2019; Roda et al., 2020; Santos et al., 2020, 2021a, 2021b). This is the example of Roda et al. (2020), who tested the coexposure effect of Cu and MPs using extremely low concentrations of MPs, and also tested environmentally realistic concentrations for Cu, and yet obtained ecotoxicological effects. On the other hand, for Jinhui et al. (2019), the low tested concentrations resulted in observations of little effects in the organisms and no vectorization of the metals (Cd, Cu, Pb) through MPs exposure. The studies reporting no effects, especially the ones using reliable concentrations are of extremely importance and should not be ignored, as they reflect the actual ecological risk of MPs (European Commission, 2019). Notwithstanding the seriousness to use low concentrations of MPs, the use of deflected amounts of metal(oid)s deserves also critical remark from scientific community. Since a few metal(oid)s exist at trace levels in seawater, real concentrations should be primarily applied, to endorse the relevance of a study aimed to address ecological risk assessment. Ultimately, SAM strongly recommend stiffening the publication criteria of scientific papers of MPs, assuring their quality, pertinence, and comparability, through prioritization of accurate studies.

7. Final remarks

The increasing release of microplastics into aquatic environment allows dissolved metal(oid)s to interact with this new particulate fraction, altering their biogeochemical cycle. Understanding the mechanisms of sorption between both contaminants can help to take measures in order to revert the environmental impact of this phenomenon. From the information collected, considering impulse mechanisms for this process, it was accomplished that weathering from environmental exposure wields mechanical, chemical, and biological action over a polymer surface promoting its reactivity. This process primarily occurs through creation of new functional groups (i.e., containing oxygen) which confer active sites allowing adsorption of metal(oid)s. Coatings (i.e., biogenic nature, organic matter, biofilms) create complexes on polymer surfaces that also allow the bond of metal(oid)s. Furthermore, the biotic and abiotic forces can cause leaching on MPs resulting in introduction of the adsorbed metal(oid)s or inherent metal(oid)s additives included during manufacturing process of polymers to surrounding water. This suggests the intervention of MPs on bioavailability of contaminants as they can contribute to transportation towards release of hazardous substances on aquatic environments and potential toxicity effects. The small size of MPs makes them reachable to all levels of the trophic chain, favoring their ingestion/contact from early life stages of organisms with higher potential toxicological impact to ecosystems. In most of the studies reported here, MPs alter the bioavailability of associated metal(oid)s either by increasing or decreasing bioaccumulation and associated effects on aquatic organisms, also caused by the MPs themselves. Time-scale exposure and concentration of the exposed chemicals state the magnitude of effects

caused in biota, with damage reported here. For this reason, chronic studies, with gradual exposure and accumulation of environmentally relevant concentrations of the toxicants will provide better information of what is factually occurring on aquatic environments, compared with acute ones. Color of polymers intervenes both in metal(oid)s content (due to be related with degree of weathering influencing sorption efficiencies and to be associated with specific additive metal(oid)s responsible to confer color to polymers) and in the uptake of MPs by species with associated effects. Old-produced plastics can be more dangerous to organisms as they have concentrated legacy contents of highly toxic heavy metals (i.e., Pb, Cd, Hg) and are highly bioaccessible through ingestion of plastic pieces, exhibiting potential higher ecological risk to aquatic environments. However, organisms were essentially exposed to virgin MPs in the majority of studies reported, what is inconsistent to what happens in natural environments, with exposure to aged ones closely representing environmental MPs, with their initial properties modified, and consequently, with adsorption capacity strengthened. Moreover, bond of polymers with metal(oid)s can differ between the elements involved, thus, a strong bond between MPs and a metal or metalloid could reduce or prevent accumulation and toxicity effects on exposed organisms. Undoubtedly, PE and PVC were the most mentioned or sampled polymers in consulted literature explored as model plastics. Due to high residual metal content of old PVC and affinity for metal(oid)s uptake, particularly Pb, PVC revealed to be the most relevant polymer regarding interactions with metal(oid)s. This polymer reunites features, as non-buoyancy and chlorine structural electronegative polar groups, that makes it a strong adsorbent of metal(oid)s, even before environmental modification on surface (although adsorption is still enhanced by weathering). Consequently, stricter rules for both use and production levels of this polymer may be required. In addition, electrostatic interaction and complexation occurring on surface of MPs were reported as most responsible to bonding metal(oid)s. In a dynamic aquatic medium, occurrence of either adsorption or desorption from/onto polymers can fluctuate, driven by water parameters (i.e., pH, ionic strength, temperature) and environmental contents (i.e., organic matter, biofilms) of water.

Trace metal(oid)s present on aquatic environments are usually highly toxic even at low concentrations to aquatic organisms, more than organic compounds (which are hydrophobic, thus, existing at low dissolved concentrations on water). Even more, surface modified polymers with environmental background either have a strong capacity to bond with metal(oid)s. Therefore, MPs could not be potentially dissociated from having metal(oid)s on their surfaces carrying them through aquatic systems to marine ones. For those reasons, they can enlarge the bioavailability of hazardous substances to aquatic biota with risk to induce ecotoxicological effects, especially if they are ingested. To clarify the ecological risk of MPs to aquic environments, more experimental studies with organisms using environmental plastic pieces at realistic concentrations, containing coatings and modified surfaces, are of great relevance.

Declaration of Competing Interest

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

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