



Review

Unfolding the interaction between microplastics and (trace) elements in water: A critical review

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ABSTRACT

Plastic and microplastic pollution is an environmental and societal concern. The interaction of plastic with organic chemicals in the environment has attracted scientific interest. New evidences have highlighted an unexpectedly high affinity of environmental plastics also for metal ions. The degree and typology of plastic ageing (including from mechanical, UV and biological degradations) appear as a pivotal factor determining such an interaction. These earlier evidences recently opened a new research avenue in the plastic pollution area. This review is the first to organize and critically discuss knowledge developed so far. Results from field and laboratory studies of metal accumulation on plastic are presented and the environmental factors most likely to control such an interaction are discussed. On the light of this knowledge, a generalist conceptual model useful for building hypotheses on the mechanisms at stake and directing future studies was elaborated and presented here. Furthermore, all available data on the thermodynamics of the plastic-metal interaction obtained from laboratory experiments are inventoried and discussed here, highlighting methodological and technical challenges that can potentially affect cross-comparability of data and their relevance for environmental settings. Finally, insights and recommendations on experimental approaches and analytical techniques that can help overtaking current limitations and knowledge gaps are proposed.

1. Introduction

Plastic litter and microplastic (MP) pollution is an environmental issue of concern. A conspicuous fraction of produced plastic waste is mismanaged and results in pollution, with freshwater and estuarine environments being mostly impacted (Bellasi et al., 2020; Koelmans et al., 2019; Nizzetto et al., 2016; Schell et al., 2021). While reports of plastic contamination in water, sediment and soil are increasingly abundant in literature (Binda et al., 2021; Crossman et al., 2020), its consequences for the ecosystem and human health are still mostly unknown.

Plastic polymers sorb organic compounds (including pesticides and antibiotics) through hydrophobic interactions, as broadly documented in scientific literature (Koelmans et al., 2016). In contrast, plastic polymers are generally considered “inert” toward aqueous metal ions. This paradigm however has been questioned by the results of recent

laboratory studies demonstrating a substantial interaction between metal ions and MPs. Metal ions are crucial micronutrients, but if over-concentrated they are among the most aggressive environmental toxicants (Johnson et al., 2017).

The nature and mechanisms of this interaction are still unclear, but sorption capacities observed for metals in laboratory settings (more than 40% of some dissolved metals are adsorbed in current experiments, Holmes et al., 2012; Lang et al., 2020) and reports of coexisting metals adsorbed on plastic particles in environmental settings (Kutralam-Muniasamy et al., 2021) warn about the likely ecological implications of MP-metal interaction (Fig. 1a), such as enhanced metal bioavailability for the biota through vector effects (Bradney et al., 2019; Naqash et al., 2020) and alteration of the cycling of elements (Seeley et al., 2020).

The number of studies focused on this environmental issues grew exponentially in the last 2 years (Kutralam-Muniasamy et al., 2021; S. Liu et al., 2021) and a few review papers were recently published on the

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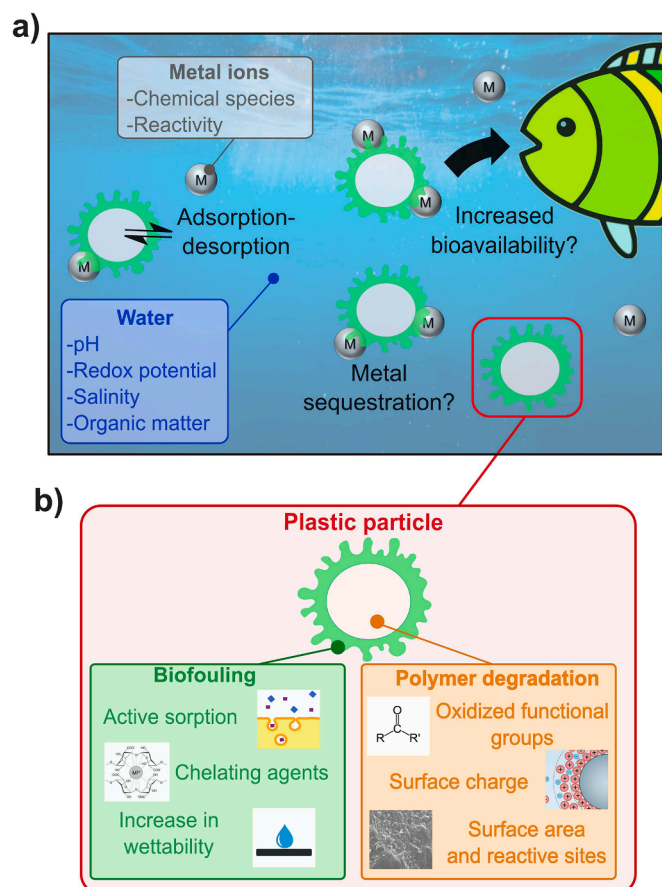


Fig. 1. a) Sketch of the main factors affecting the interaction of plastic particles (indicated by the white spheres with the green corona) and the metals (indicated with the grey spheres) in the water environment and the possible environmental implications (e.g., possible vector effects and metal sequestration). b) A focus on the main phenomena affecting polymer degradation in water environment and possibly enhancing plastic-metal interaction, including the effect on the plastic particle surface (represented by the white sphere) and the colonization of plastic particles by microorganisms (represented by the green corona in the sketch). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

interaction between plastic particles and chemical contaminants (Liu et al., 2020; Torres et al., 2021; Vieira et al., 2021), but mainly dealing with the ecotoxicological implications (Bradney et al., 2019; Cao et al., 2021; Naqash et al., 2020; Verla et al., 2019). The diversity of experimental approaches and materials used to analyze MP-metals interaction and lacking of conceptual models for hypothesis creation have hindered progresses in the ability of understanding and predicting the MP-trace element interaction process.

In this critical review, we face this challenge with the goal of providing information on the state of the art of research on the topic, highlighting knowledge gaps and delivering insights useful to guide future theoretical and experimental assessments of the interaction between metal ions and plastic. This review work is structured in three parts. In the first part (described in Section 2 of the paper) we will present and discuss the current knowledge on the role of plastic-side and water-side determinants controlling adsorption-desorption equilibria, dynamics and thermodynamics of the plastic-metal ion interaction. Such a review includes an account of currently available evidences on the role of plastic ageing and of water physicochemical properties. In Section 3 of the paper different conceptual models of the metal ion-plastic interaction will be proposed considering variability of characteristics of weathered plastics, stemming from both the influence of thermo-

oxidative degradation processes and formation of biological films. Finally, Section 4 of the paper will be dedicated to the review and critical discussion of current experimental approaches to study this interaction in both laboratory-simulated conditions (bottom-up) and in environmental samples (top-down).

2. Processes and conditions at the interface between plastics and metals

Analyzing plastic-metal ion interaction from a mechanistic point of view requires handling a complex array of synergistic and competitive processes, occurring both in the solution and at the interface between the polymer and the water phase. Both these are expectedly modulated by water chemistry on the one side (mainly salinity, pH, temperature, redox conditions and other dissolved ions), and the characteristics of the plastic matrix on the other side (with a major role played by the degradation rate and biofouling of polymers, which influence surface charge, wettability and reactive surface area; Fig. 1b). In the following sections the environmental processes which can influence the modality of plastic and metals interaction will be reviewed, focusing on the challenges concerned with their experimental assessment and on the possible approaches to overcome them.

2.1. The plastic-side: polymer degradation and its possible effects on the interaction with metal ions

The level of plastic ageing is reportedly an important factor for metal sorption. Two main processes are responsible for altering plastic properties at the interface with the environment: physicochemical deterioration and biological colonization. Pristine plastics are composed by an amorphous or semicrystalline matrix of entangled polymer chains (the most used include polyethylene - PE, polypropylene - PP, polystyrene - PS and polyamides - PA) with the intramolecular space typically filled with chemical additives used to improve physicochemical and mechanical properties. Additives includes, for example, plasticizers, antioxidants, light quenching compounds, flame retardants and dyes. The topic of polymer ageing on metal sorption is widely studied (Bellasi et al., 2020; P. Liu et al., 2021; Lv et al., 2015; W. Wang et al., 2019). The sketch in Fig. 1b represents the two main processes affecting ageing of plastic particles dispersed in the environment. Plastic surface can be altered by physicochemical modification in water bodies, affecting the surface charge and oxidation; moreover, pristine or aged plastic can be colonized by different microorganisms which completely alter the surface of polymers, possibly enhancing an interaction with (trace) elements through increasing wettability, and exposing charged groups carried by extracellular polymeric substances typical of biofilm-forming microorganisms.

The potential influence of plastic ageing in enhancing the interaction with metal ions in water has been recognized and investigated in recent studies (Table S1 in Supplementary Material). Adsorption-desorption tests with metals have been conducted on plastics with different level of ageing (Lang et al., 2020; Thomas et al., 2020; Q. Wang et al., 2020). Chemical oxidation processes (especially UV-based) have received more attention, while the role of biological colonization in affecting sorption of metal ions have been partly overlooked. While decomposing a system complexity in its constituents is often a good approach to research, it must be reinforced that in environmental settings chemical and biological ageing co-occur and can affect each other, hence minimalistic experimental approaches may not be sufficient to fully elucidate the system behavior. Hence multi-tiered experiments at increasing level of system complexity can represent the way forward. For example, there is a clear demand for developing a better knowledge on the synergic role of biological colonization and chemical ageing of plastics as determinants of the capacity and dynamics of metal ion sorption on the plastic substrate (Lucas et al., 2008). It was reported that the mechanical ageing of polymers can further enhance the biofilm colonization rate (Carson

et al., 2013). Hence studies that focus on such an interaction can produce data with a higher environmental relevance. In the following sections, we will present the state of the art on the mechanisms and processes determining physicochemical and biological alteration of plastics and provide insights on their potential role in enhancing sorption of metal ions.

2.1.1. Physicochemical degradation

Physicochemical processes mainly responsible for the ageing of plastics are mechanical deterioration and chemical (photo-oxidative) processes. Mechanical deterioration is mostly responsible for the formation of micro-cracking, which promotes the fragmentation of polymers in smaller particles (Ren et al., 2020). This process that can be caused by several environmental phenomena, including: abrasion with the substrate (e.g., driven by bioturbation, waves, or currents), thermic stress, UV radiation and deterioration by currents and waves (Min et al., 2020). Moreover, these phenomena can drive the leaching of additives like plasticizers, causing loss in mechanical resistance and elasticity of plastic materials, further enhancing degradation processes (Paluselli et al., 2019). Mechanical deterioration results in micro and macro fractures of the polymer matrix that determine increased surface rugosity, increased specific surface area (which in turn results in higher adsorption rate of metals, Dong et al., 2020; Luo et al., 2020) and can develop into fragmentation of plastic debris in increasingly smaller MPs.

Physical deterioration of plastic can also be promoted by oxidative reactions that, at molecular level, take place by breaking cross-links between polymer chains or cause polymer chain interruption. With time these alterations at molecular scale can propagate and impair plastic integrity at a macroscale, altering its physical-technical properties and making it prone to further physical deterioration and fragmentation. In the environment such a degradation is typically due to photo/thermo-oxidative processes. UV radiation is the most common driver of polymer oxidation (Bracco et al., 2018; P. Liu et al., 2021). This process initiates with photonic or homolytic cleavage of C—C or CH bonds, or more frequently of the -O-OH links of hydroperoxides present in the amorphous zone of polymers from the manufacturing process. These events produce alkyl (R•) or alkoxy (RO•) macroradicals, respectively. In the case of R• the reaction terminates with the formation of vinylene double bonds, while RO• lead to formation of ketones, esters, and carboxylic acids (Brandon et al., 2016). In environmental condition the formation of hydroperoxide radicals in presence of molecular oxygen can play a key role in the propagation reaction (Bolland Cycle, Bolland and Ten Have, 1947) to form peroxide radicals (ROO•) branching the kinetic chain towards production of ketones, alcohols, esters and acids. Because of the role of molecular oxygen, the formation of oxidized terminations is likely to proceed from the surface of plastic (at the interface with oxidic water environments) extending in amorphous regions. These chain reactions can affect the sorption properties of MPs because the generated oxygen-containing groups increase polarity, hydrophilicity and the surface charge (Liu et al., 2020). Oxidized functional groups can ultimately act as binding sites for inorganic ions (P. Liu et al., 2021; Song et al., 2017).

2.1.2. Biofouling and biological colonization

Polymers widespread in aquatic environments represent a suitable substrate for the growth of organic and biological films (Leiser et al., 2020; Lobelle and Cunliffe, 2011). Deposition of priming organic films on the surface of plastics in water is rapid (i.e., few days; Harrison et al., 2014; Pinto et al., 2019). This is a passive and spontaneous uptake process driven by the Brownian diffusion of organic compounds dissolved in water (e.g., colloids, humic substances) in the water-side thin boundary layer and the sorption onto the plastic surface by weak molecular interactions. From the molecular point of view, these interactions can have a variable nature given the diversity of functional groups on aged plastic and the complex mixture of organic compounds in natural waters. The chemical properties of natural priming films are

determinant for the following process of macrofouling (colonization by microorganisms, Lorite et al., 2011). Many bacteria strains display the ability of anchoring to diverse substrates and form biofilms as an evolutionary adaptation. In order to do this, they can regulate cell walls and the hydrophobicity of the membranes, extracellular polysaccharides composition and develop dedicated structures such as pili, curli, fimbriae and flagella to exploit adhesive properties of primed surfaces (Rummel et al., 2017).

Composition of bacterial communities on plastics can vary dramatically (Pinto et al., 2019). The colonization of microorganisms on surface is an example of ecological succession, where the assembling of the biofouling community progress with time and it is determined both by neutral (e.g., random) and niche (e.g., driven by ecological interactions with the environment and other organisms in the community) processes. This process is generally slower than priming, considering that: i) microorganisms that can adhere on the plastic substrates are most likely less abundant than dissolved organic matter (DOM) in the water solution and ii) there is the need of successful anchorage of a certain number of organisms for an effective biological colonization. The initial phase of the biofilm formation is likely a random process, whereby the first organisms that can successfully anchor and grow on the substrate will determine the progress of the succession and the resulting biological and chemical characteristics of the film. Biofilms affect the interaction of plastic particles with (trace) elements, as they enhance plastic surface wettability (Dussud et al., 2018), actively accumulate metal ions through transmembrane transport (Geng et al., 2019) and present extracellular polymeric structure that can form chemical complexes with metals (Y. Wang et al., 2020; see also Section 3.2).

Differences in the biofilm composition can also be determined by niche processes and therefore reflect different environmental conditions and water chemistry (Leiser et al., 2020; Nava and Leoni, 2021; Pinto et al., 2019). This in-turn can likely influence affinity for metal ions. Obtaining a representative and reproducible experimental model of a biofilm to carry out controlled experiments of plastic-metal interactions is therefore a critical challenge. Previous works have shown that prokaryotes can initiate formation of biofilms with a secondary colonization by eukaryotes, including protozoa and microalgae (Mistic and Covazzi Harriague, 2019). These organisms have very different membranes and cell walls characteristics, as well as contrastingly different physiology. Therefore, they most likely show different types of interaction with metal ions. Differently, it has been reported that polymer type scarcely affect biofilm species composition (Zhang et al., 2021).

2.2. The water-side: influence of temperature and water chemistry

In this section, the available knowledge on the influence of water physicochemical properties on the interaction between (trace) elements and plastics is presented, with a specific focus on environmentally relevant conditions. The scope of this part of the review is to identify knowledge gaps and limitations of current experimental approaches and to list the water-side variables playing an important role in the interaction.

2.2.1. pH

The effect of water pH on the plastic-element interaction has been the focus of some experimental assessment. pH is in fact known to affect metal ion speciation and the surface properties of polymers. The surface of most common polymers in the environment (e.g., PE and PP among others) have low pH values of point of zero change, meaning that at the pH of common water environments the surface is electrically negative, with an increasing negative charge at increasing pH also at environmentally relevant conditions (Lin et al., 2021). Moreover, surface properties of polymers carrying ionizable functional groups (and in particular of oxidized plastics) will change in dependence of pH. Ionizable functional groups exposed to the solution will become deprotonated at increasing pH values, increasing also the number of reactive

domains available for the binding of metal ions (Tang et al., 2020). While these polymer-side influences of water pH on plastic reactivity has been experimentally confirmed for a range of polymers (both pristine and aged, including PE, PP and nylon; Ahechti et al., 2020; Tang et al., 2020), water pH is most likely to affect the plastic-metal ion interaction through controlling metal speciation in the solution with important consequences on their affinity for binding sites on the plastic surface. In fact, pH influences the degree of ionization and distribution of the metal species in solution (F. Wang et al., 2019). Experimental results showed that the effect of water pH in determining the sorption of metal onto polymers varies depending on the cationic or anionic nature of dissolved species. The adsorption of bivalent metal cations (e.g., Cu, Cd and Pb) onto different polymers increases as pH raises, as shown in several experimental studies (Ahechti et al., 2020; Guan et al., 2020; Tang et al., 2020; Zou et al., 2020). Such a trend may be explained as follows: when pH is low, H^+ competes with the metals (electrostatic repulsion) for the adsorption sites, negatively affecting the metal adsorption rate.

Anionic species show the opposite behavior. The adsorption decreases with increasing pH of the medium: at low pH, the OH^- concentration is low and it does not compete with anion for adsorption in positively charged domains of the polymer. Holmes et al. (2012) and Zhang et al. (2020) showed in fact that whereas the adsorption of Cd, Co, Ni and Pb increases with increasing pH, Cr adsorption decreases since it exists in solution in the oxyanionic form ($HCrO_4^-$ and CrO_4^{2-}). Likewise, the study of Dong et al. (2020) seems to confirm these effects for As (III) adsorption on PS MPs, observing that as pH of the solution increases, the form of As(III) changes from H_3AsO_3 to AsO_2^- .

It should be noted that these observations were made in controlled artificial systems that excluded the presence of other chemical species or ligand in solution, which are instead important constituents of natural water environments. These observations were conducted therefore through oversimplified approaches where only metals and pH adjusters and buffers (typically HNO_3 , NaOH and $NaNO_3$) were present. It must be noted that, especially in the case of alkaline environments, sulfates and chlorides used to adjust pH can easily form insoluble salts with the dissolved element, making it not available for adsorption by plastic, hence potentially affecting the metal ion activity in the solution and the experimental assessment of distribution coefficients.

Moreover, while experimental works has broadly focused on sorption kinetics, the effect of pH on the desorption mechanism has so far been scarcely considered (see Section 3.1). It can be expected that desorption of metals from plastics (as from different other solid media) could be favored in acidic pH, which facilitate formation of free ions (Kalcíková et al., 2020). This is indeed an important process relevant for the bioavailability of metal following ingestion of contaminated plastics fragments by organisms. The acidic gastrointestinal tract of most aquatic organisms may indeed promote speciation of plastic-bound metals into more available and toxic forms, directly inside the organisms, embodying the trojan horse effect (Smith and Turner, 2020).

2.2.2. Salinity

The salinity of the medium can alter the adsorption of metal ions onto oxidized or biofouled plastic surfaces. Increased ionic strength of the solution can enhance competition of metals with other dissolved ions for binding sites and can influence accessibility of these binding sites. According to most studies, the adsorption of positively charged ions is inversely related to salinity: as salinity increases, metal species and Na^+ ions compete for the adsorption onto plastics. This has been observed for Pb, Cd, Zn and Cu (Fu et al., 2020; Holmes et al., 2012; Tang et al., 2020; Turner and Holmes, 2015; F. Wang et al., 2019). The presence of Cl^- may also promote formation of Cl-transition metals homoleptic complexes and hydrates, possibly leading to a lower activity of free metal ions in the solution and lower adsorption. This effect was observed so far for Cd (F. Wang et al., 2019). While the influence of salinity on the metal ion-plastic interaction has been recognized, there is a need to elucidate these processes in the context of more environmental realistic settings,

whereby a number of inorganic ionic species are engaging in the competition. For example, major ions such as Ca^{2+} , Mg^{2+} , K^+ , NO_3^- and SO_4^{2-} can compete with specific cationic or anionic species of trace elements, or form salts with them, inhibiting their binding with plastics (Fu et al., 2020). It has been argued (Zhou et al., 2020) that the competition between similar bivalent metals negatively affects the adsorption.

Beyond the water-side effects on metal ion speciation, salinity can also influence plastic-side properties by effecting the electric double layer expected to form over the surface of weathered and partially charged surfaces. This process is postulated by the Derjaguine-Landau-Verwey-Overbeek theory. The electrical double layer is a structure on the surface of an object exposed to a fluid constituted by two parallel layers of charge surrounding the object. The first layer, the surface charge (either positive or negative), consists of ions adsorbed onto the object due to chemical interactions. In the case of aged plastics this can be the carboxylic, ketones groups of oxidized polymer chains, or of the exopolysaccharides of microorganisms in coating biofilms, and the different ions non-covalently bond to them. The second layer, also called "diffuse layer", is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer. The diffuse layer is loosely associated with the object and it is made of freely dissolved ions moving under the combined influence of electric attraction and thermal Brownian motion.

At varying solution salinity, the thickness of the double layer can vary likely influencing the rate of diffusion and sorption of dissolved ions onto the binding domain on the particle surface. Furthermore, the thickness of the double layer has also implications for the tendency and the rate of homo and hetero aggregation of small particles (including, for example, nanoplastics present in solution). At increased ionic strength of the solution, the electrical double layer of these particles can be compressed reducing repulsive forces, leading to aggregation with other similar particles or with naturally occurring colloids (Singh et al., 2019; Wu et al., 2019). Aggregation alters the physical properties of the particles (for example making them to precipitate) and the amount of surface available for interaction with dissolved species per unit of particle volume. This, in turn, can result in reduced adsorption capacity for metal ions, by the unit of mass of plastic suspended in a solution.

2.2.3. Temperature

The influence of temperature has been so far considered for the investigation of thermodynamic equilibria of the metal ion-plastic interaction. All the experimental studies found such an interaction to underpin a negative variation of Gibbs free energy ($\Delta G < 0$) and be therefore spontaneous. In most cases this process was also found to be endothermic with a positive entropy change ($\Delta H > 0$). These findings are based on a series of observations conducted with Cu and Zn to polyethylene terephthalate (PET, Q. Wang et al., 2020), with Cu on polyurethane (PU, Xue et al., 2021) and with Pb on nylon, polyvinyl chloride (PVC), PS and PE (Lin et al., 2021; Tang et al., 2020). Differently, studies with As(III) adsorption to PS MPs highlighted an exothermic ($\Delta H < 0$) reaction (Dong et al., 2020).

These experiments were conceived to study the thermodynamics of the metal ion-plastic interaction in "ideal" conditions and shed light on fundamental mechanisms underpinning the chemical physical interaction (see also Section 3.2); applicability of the measured activation energies and enthalpies in real environmental settings is uncertain. Main confounding factors link to the complex nature and great variability of the characteristics of chemically or biologically weathered plastics in the environment and on the role of competing interactions (i.e., binding with other dissolved ligands, likely DOM or major ions) taking place in the water-side in natural conditions (Smith and Martell, 1987). Moreover, also the effects of the environmental range of temperature (e.g., 5–25 °C) should be tested not only for adsorption but also desorption processes (similarly to pH, Section 2.2.1), being this a process overlooked in experiments conducted so far.

2.2.4. Dissolved organic matter (DOM)

To evaluate the interaction of plastic with metal ions in a realistic environmental context, experiments with variable levels of dissolved organic matter have been performed. Dissolved organic matter can bind dissolved metals (Caprara et al., 2016; Martell et al., 1988; Plöger et al., 2005) and can therefore synergistically or antagonistically modulate metal adsorption onto plastics. Organic matter in water can form complexes with metals and therefore lowering the metal dissolved ions activity (Liu et al., 2020). However DOM can also be adsorbed on plastic, both through hydrophobic interactions or through weak interaction with charged or partially charged functional groups (the formation of priming organic films onto plastic in water environments is an example of such a process), possibly enhancing the accumulation of metals on the plastic surface through the deposition of metal-organic matter complexes or by increasing the density of negative charges on the primed plastic, and consequently affinity for metal ions (Li et al., 2019). Moreover, once metal ion-DOM complexes are formed in the solution-phase, their reactivity changes compared to dissolved metal ions, possibly enhancing hydrophobicity and, consequently, the likelihood of adsorption on neutral plastic surface (such as, among others, the surface of pristine PP and PE, Tang et al., 2021).

Because of such a complexity, earlier studies yielded sometimes contradictory results. For example, Tang et al. (2020) proved that fulvic acid in the solution negatively affected the adsorption of Pb onto aged nylon MPs, possibly due to complexation between fulvic acid and Pb (through interactions with carbonyl, hydroxyl and carboxyl groups). A similar behavior was observed with humic acid, competing with different microplastic polymers for Cd adsorption (Zhou et al., 2020).

In contrast with these results, Fu et al. (2020) and Godoy et al. (2019) observed an increase adsorption Pb, Cr and Cu on different polymers in tap water and wastewater (compared to distilled water) proposing the interaction was enhanced by DOM present in these matrices.

These controversial results are possibly linked to the challenge of conducting factorial experiments in ternary systems (i.e., in presence of plastic, metal ions and DOM) with the factors not being fully independent and prone to interfering with each other in a number of possible ways. To disentangle such a complexity, focus should be placed in analysis of the behavior of the interaction terms resulting from the factorial experiment result, on varying experimental conditions. While this may help to shed lights on the mechanisms of the three-way interaction, such an analysis was not fully addressed in earlier studies. Moreover, existing studies on the role of DOM on (trace) element-plastic interaction used different time lags for equilibration, without focusing on possible different kinetics in adsorption caused by complexing agents in the systems. Suggestions for future studies include the speciation analysis of elements in solution, considering equilibration and different kinetics of adsorption desorption of complexes related to free metal ions (see also Section 4.2.2).

2.2.5. Organic pollutants

In some very recent studies the effect of dissolved metal ions and some organic pollutants (e.g., surfactants, Zhang et al., 2020; phenanthrene, Zhou et al., 2020; antibiotics, Y. Wang et al., 2020) co-occurring in water environments were investigated. The main rationale for these studies was to reveal potential competition among these species for binding sites on the plastic. In realistic environmental settings the outcomes of such competition will be primarily determined by the concentrations of the different species (which can vary across orders of magnitude) rather than their affinity for a given binding domain. Studies conducted so far considered instead exposure scenarios with extremely high concentrations of organic and inorganic contaminants (in the order of mg/L), often in absence of other dissolved ligands or major ions and in solutions with controlled ionic strength and buffered pH. Hence, current understanding of the interaction of metal ions and organic contaminants for the sorption on plastic is insufficient to draw expectation of their relevance for the environment. It is suggested that assessing

plastic/water phase distribution of major organic and inorganic contaminants in environmental settings (e.g., from monitoring studies) could provide useful insights to elucidate the importance of possible competing effects for binding sites, and rank plastic affinity for pollutants to support ecological risk assessment.

2.2.6. Other potentially interesting water-side variables

Redox potential of the water medium can affect the speciation of trace elements in water and their equilibria between solid and liquid phases (Binda et al., 2018; Borch et al., 2010). It can affect the surface charge of polymers (Liu and Bard, 2009) determining the oxidation of functional groups at the surface of plastics (Wu et al., 2017). It can also influence growth and biological composition of film covering plastic surfaces (Niu et al., 2021; Rogers et al., 2020). These features have possible direct or indirect effects on the capacity of plastic for metal ion adsorption.

Redox potential typically varies along the water column and at the interface with sediments. In light and oxygen depleted conditions the environment tend to become reductive (Niu et al., 2021), hence plastics in the anoxic waters or sediments of meromictic environments will expectedly have different interaction with metal ions, compared to those in the oxic zone. Despite its potential importance, the redox potential of the medium has been so far overlooked in experimental assessment of the metal-plastic interaction.

The amount and typology of suspended solids in water is also a potentially important determinant of metal accumulation on plastic. Suspended solids play an important role on speciation and mobility of dissolved metals. A recent study by Guan et al. (2020) assessed adsorption of metals and compared natural suspended sediments from different lakes with those of plastics (PS particles, both virgin and naturally aged in lake water) showing the higher efficiency of the earlier. Another recent work by Li et al. (2019) found similar results using sewage sludge as a competitor of plastic for metal ion adsorption. Future studies should include ternary systems with varying concentration of plastic particles and other solid matter to understand how the competitive effects of other natural adsorbents reduce plastic adsorption capacity.

3. Models of plastic-metal interaction and their applicability for environmental settings

In this chapter proposed mechanisms of plastic-metal interaction are reviewed on the bases of available experimental evidences and measurements of rates and reaction energies. To the best of our knowledge, only few studies performed preliminary model fitting to explain the interaction between plastic and metals (Guo and Wang, 2021; Town et al., 2018), while this issue was better elucidated and reviewed for organic compounds (Koelmans et al., 2016; Mosca Angelucci and Tomei, 2020). While reviewing the proposed models, possible limitations for their applicability in the environmental context will be listed. Finally, conceptual frameworks will be presented drawing from the synthesis of currently available studies that can be useful for describing the interaction in more general and, at least, semiquantitative terms.

3.1. Experimentally derived models of interaction

The interaction of MPs and metal compounds in water environments is typically modeled by statistically fitting results of kinetics and equilibrium isotherm experiments (e.g., Desta, 2013; Langmuir, 1916). The evaluation of the kinetics and equilibria of reaction enable the elaboration of mechanistic frames to describe the processes controlling physical transport of the metals at the interface between plastics and water, and an estimation of the energy of reactions. This in-turn provides useful information for generating hypotheses on the molecular bases of the process. These models enable listing the most plausible physical (physisorption) or chemical (e.g., complexation) mechanisms

interaction between dissolved metals and MPs in water solutions.

Thermodynamic parameters are usually extracted from experiments in which plastics are exposed to metal ions in a buffered water solution at constant physicochemical conditions (salinity, pH, temperature) in closed systems. The experiment proceeds for an amount of time, sufficient for the system to reach equilibrium, with constant and stable concentration of ions in the water and plastic. Experiments can be repeated at varying initial metal ion concentration in the dissolved phase, in order to evaluate non-linearity of the sorption curve, or at varying temperature to study shift of equilibrium and evaluate in turn the energies of reaction.

Kinetic models are instead fitted contacting one batch of MPs suspended in solution with a given concentration of the studied element(s) and analyzing the element(s) in solution at regular time intervals (experimental details in Section 4.2). They aim to analyze the limiting step in adsorption process (Guan et al., 2020; Mosca Angelucci and Tomei, 2020).

On an ultramolecular level, plastics are relatively inhomogeneous materials with crystalline regions (where polymer chains are regularly lined up) and amorphous regions (where polymer chains are not lined up). Amorphous regions of the polymer are in fact disordered and more permeable than crystalline ones (Bradney et al., 2019; Velez et al., 2018). Given that sorption experiments are typically conducted with plastic specimens in the (at least) micrometer or mm range, the matrix can typically include both amorphous and crystalline portions, introducing an inherent confounding factor. The Langmuir or Freundlich models are the most common frameworks used to fit adsorption isotherms: the Langmuir model has been applied to fit adsorption of metals in the crystalline regions; the Freundlich model was instead applied to model interaction in the amorphous region as it overcomes the assumption that all binding sites are homogeneously distributed on the surface and are energetically equivalent. While these models provided good fitting results in describing equilibria in simplified experimental conditions (Fu et al., 2020; Godoy et al., 2019; Holmes et al., 2012), they appeared to be too simplistic for a potential environmental application. In fact, when compared with more complex equilibrium models (such as the Temkin, Xuan Guo et al., 2020; Sips, Xue et al., 2021; and the Liquid-solid extended BET isotherm model, Lin et al., 2021), Langmuir and Freundlich models showed a lower performance. These experiences however converged in showing that equilibrium isotherm curves are not linear, suggesting that (at least in the simplified experimental scenarios) surface interaction and adsorption are the driving mechanisms, while diffusion in the polymer matrix is a negligible process (Mosca Angelucci and Tomei, 2020).

Similarly to equilibrium models, more simplistic kinetics models such as pseudo first order and pseudo second order (Fernández et al., 2020; Zhou et al., 2020) often do not well describe the experimentally observed adsorption kinetics, indicating that the adsorption is a complex and multistep process. Different models are recently considered, such as the shrinking core model, tested for Cu, Ni and Zn on nylon (Tang et al., 2021); or the external and internal mass transfer, found as good descriptors for Sr on PS, PA and PP (Xuan Guo et al., 2020), for Cu on virgin PE (Y. Wang et al., 2020) and for Pb on PVC, PS and PE (Lin et al., 2021).

The analysis of isotherm adsorption at different temperatures enables estimating enthalpies of adsorption (Table 1), which give critical insights in the mechanism reconstruction. Generally, results of enthalpies confirmed that physical adsorption is the main mechanism responsible of interaction at least with plastics with no biofilm coating. Most of the estimated ΔH values were in fact smaller than 40 kJ/mol (Lin et al., 2021; Tang et al., 2021). There is, however, an important exception. The study of As adsorption on PS showed a slightly negative estimated ΔH value, indicating an exothermic process for binding. In this case, in fact, a chemical binding through hydrogen bonds was hypothesized (Dong et al., 2020).

An inherent limitation of these models is their uncertain relevance to describe plastic-metal interaction in environmental settings. Models are

Table 1

Fitted enthalpies and Gibbs free energy from isothermal models performed in literature, including used polymers and ions for the equilibrium experiments.

Polymer	Element	Experimental ΔG (kJ/mol)	Experimental ΔH (kJ/mol)	Reference
PU	Cu	-7.87; -8.89; -9.73	8.61	(Xue et al., 2021)
PVC; PE; PS	Pb	-8.87; -9.41; -9.96 (PVC); -3.23; -3.84; -4.44 (PS); -13.11; -14.07; -15.03 (PE)	6.85 (PVC); 14.17 (PS); 14.6 (PE)	(Lin et al., 2021)
Nylon	Cu; Ni; Zn	-12.19; -13.79; -15.38 (Cu); -9.17; -11.21; -13.25 (Ni); -10.63; -12.00; -13.37 (Zn)	33.75 (Cu); 49.54 (Ni); 28.77 (Zn)	(Tang et al., 2021)
Nylon	Pb	-1.49; -2.52; -5.2	41	(Tang et al., 2020)
PS	As	-2.35; -2.22; -1.96	-8.02	(Dong et al., 2020)
PET	Cu; Zn	-21.401; -23.114; -24.229 (Cu); -21.458; -22.621; -23.537 (Zn)	19.428 (Cu); 8.514 (Zn)	(Q. Wang et al., 2020)

in fact determined through fitting data from minimalistic experiments with anomalously high concentration of trace elements and unrealistic boundary conditions (e.g., lack of ligands or other competing ions in the solution phase, absence of biofouling). These critical issues will be more specifically described in Section 4.2. The combination of kinetics and equilibrium modeling however helped to gain mechanistic insights on the processes responsible for adsorption of ions, which, under the studied experimental settings, appear to be embodied by one or more types of weak electrostatic interactions (Dong et al., 2020; Fu et al., 2020; Zhang et al., 2020).

Few studies focused on assessing which functional group on the plastic surface is mainly responsible of the electrostatic interaction with metal ions using computational chemistry simulations (Dong et al., 2020; Xuan Guo et al., 2020; Y. Wang et al., 2020). It has been observed that the density of oxygen containing chemical groups (e.g., hydroxyl, carboxyl) on the surface of plastic affect sorption equilibria. Other secondary physical processes proposed to investigate the adsorption phenomena are π - π interactions (Xuetao Guo et al., 2020; Zhou et al., 2020) and physical diffusion (Town et al., 2018; Y. Wang et al., 2020).

In contrast to physical interaction, chemical bonds are rarely observed, and these principally include the complexation of metals on plastic surface and hydrogen bonding (Guan et al., 2020; Y. Wang et al., 2020). However, it is worth considering that chemical bonding in an environmental context results a more stable process, especially considering a natural competition with other ions (Ho and McKay, 1998).

Considering the environmental applicability of the abovementioned models, a gap in the research conducted so far on metal sorption on plastic is the lack of experimental focus on the determination of desorption rates. In natural settings (especially in water compartments) equilibrium is a rare event due to temporal variability in ion concentration, water chemistry, temperature, hydrology, etc. (Mosca Angelucci and Tomei, 2020). Considering their weak nature, metal ions-plastic interactions take place to a dynamic exchange, where ions are continuously exchanging across the interface between the solid phase and water (F. Gao et al., 2019).

The studies that addressed the reversibility of metal ion sorption on plastic focused on extractability of adsorbed elements in simulated animal and human gastro-intestinal fluids (e.g., Holmes et al., 2020; Liao and Yang, 2020; Turner, 2018), while desorption in milder (environmental) conditions was only very recently considered in two studies (Fernández et al., 2020; Zhou et al., 2020). The recent work by Zhou

et al. (2020), in particular (to the best of our knowledge), is the only which explored mathematically the adsorption-desorption equilibria. These studies confirmed the weak bond forming between plastic and metals, with desorption occurring at a high rates and mild conditions. These findings can have important ecological implications considering the possible interaction of MPs, which are known to move through the water column and interact with the biota.

Finally, it is important to note that none of the sorption experiments listed in Table 1 has been conducted with biologically coated plastic (which might be prevalent in the environment). In this case, the type of interaction is expectedly very different, as microorganisms can uptake and use metals as nutrients through active transmembrane transport (S. Liu et al., 2021). Also, extracellular structure on bacterial surface may hold domains capable of forming more stable complexes with metal ions.

3.2. A conceptual framework for future investigations

Considering the highlighted limitations and little environmental realism of the interaction models developed so far, it is useful to introduce a more holistic conceptual frame to guide future experimental studies. In the following paragraph such a framework is described in a tiered approach with three levels of increasing complexity: pristine polymers, chemically weathered polymers and biofouled polymers.

The random-coil model provides a useful frame to describe polymeric materials on a supermolecular level. Based on this model, polymer chains have a random and strongly entangled arrangement through non-permanent physical crosslinks (see Fig. 2a). Common polymers of environmental relevance are either completely amorphous or semicrystalline. In semicrystalline regions chains are aligned. In glassy amorphous regions, instead, polymer segments can move locally, and such a process can assist diffusion of small molecules. In connection with diffusion, amorphous polymers are characterized by a large free volume exceeding 10% of the bulk volume. Chemical species of available metals, on the other hand, can be modeled depending on pH-pE conditions: different speciation models are currently available in literature for their modeling (e.g., Guan et al., 2020).

In case of pristine plastic items, the characteristics of the plastic surface is expected to reflect the hydrophobic nature of the polymer aliphatic chains (e.g., in case of PE and PP). At neutral-acidic pH and in absence of complexing or charged domains on the plastic surface the deposition of dissolved metal ions is disfavored by solvation energy. In case of some polymers (e.g., PS) the weak π - π interaction between metal ion and aromatic ring (expected ΔH between -5 and -20 kJ/mol), as well as complexation with phenyl groups (expected ΔH between 20 and 50 kJ/mol) are in principle possible, although unlikely to happen in an environmental context (Zhou et al., 1998). Chemical additives present in pristine plastics can in principle affect kinetics and thermodynamics of interaction and their role should be analyzed in future studies.

The surface of oxidized plastic, instead, can present i) alkyl groups capable of forming coordination complex with metals, and ii) oxidized groups that can act as permanent dipoles and form noncovalent interactions with metal ions in environmental conditions (Fig. 2b). In these conditions, the higher adsorption rate observed experimentally will vary in correlation with the quantity of surface oxygen containing groups. Expected equilibrium constant of these interactions will be ΔH ranging 10 – 20 kJ/mol for PE or PP, and between -5 and -20 kJ/mol for PS and 20 – 50 kJ/mol for Nylon. Mass transfer models will be better descriptors of interaction kinetics because of presence of different binding groups on the plastic surface that can become saturated in different stages and rates.

The accumulation of metals on plastic surfaces coated with biofilms is, finally, expected to be underpinned by very different processes and energies (Fig. 2c). The development of biofilm on plastic has been observed to vary from 5.5% after 15 days to 54% after 90 days of incubation (Ahamed et al., 2020). Owing to their long residence time in

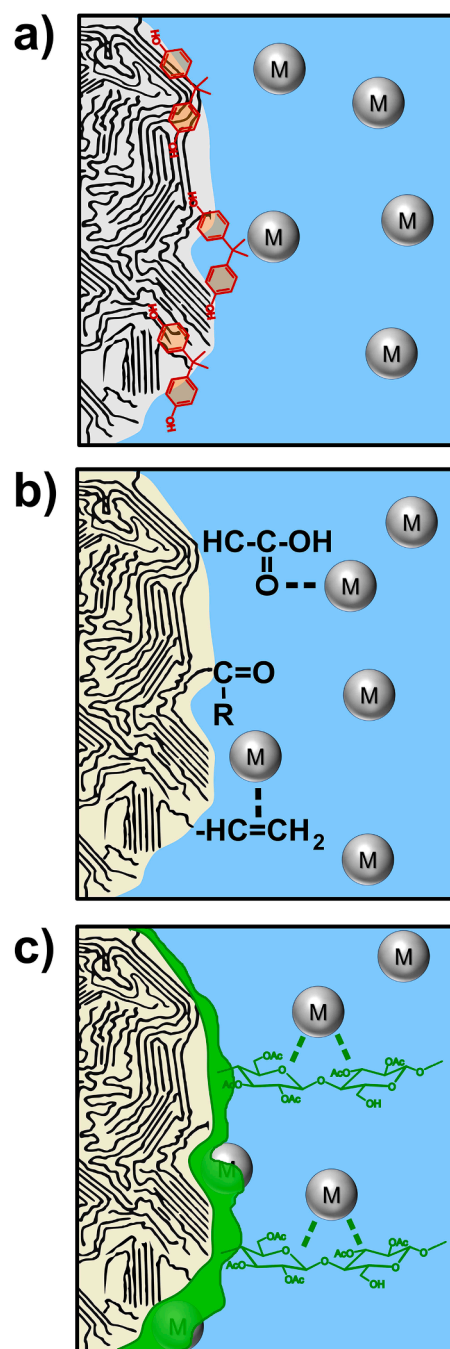


Fig. 2. Three sketches of the conceptual models proposed in this review. a) Pristine plastic particles: very unlikely interaction with dissolved metals (as M in the picture). Only the chemical additives (indicated in red) can possibly mediate a chemical interaction. b) Aged plastic: the interaction is likely through electrostatic attraction, especially to oxygen containing functional groups of the polymer. c) Biofouled plastic: the biofilm-covered plastic present a completely reshaped surface reactivity. Active biosorption process can likely happen in the cellular membranes and extracellular polymeric substances (e.g., polysaccharides) possibly chelate metal ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the environment, most plastics found in water environments are likely to be coated by a biological film, and their surface properties and reactivity must be strongly mediated by the characteristic and biological activity of the biofilm itself.

While the effect of biofilms was only recently considered for plastic

particles (Ahamed et al., 2020; Guan et al., 2020; Y. Wang et al., 2020), several studies have shown that biofilms efficiently accumulate metals (with enrichment factors ranging 500:1 - 6000:1). The underlying mechanisms of such an active uptake process are well studied (Ancion et al., 2010). These involve both cell wall sorption and active transmembrane transport followed by intracellular accumulation (Geng et al., 2019; S. Liu et al., 2021). Anionic polysaccharides typical of the bacterial capsule have a strong affinity for metal counterions, even at low concentration (Fig. 2c), possibly originated from evolutionary adaptations specifically for optimizing acquisition of these essential micronutrients.

Microbial cell walls contain numerous anionic functional groups (-COOH and P-O_3^{2-}) and the extracellular polymeric substances (a major component of biofilms) are composed of several natural polymers (e.g., lipids, polysaccharides, proteins) with negatively charged functional groups like hydroxyl (OH^-) and sulfate (SO_4^{2-}) that can enhance complexation of metal species (Ahamed et al., 2020).

Microbiota composing the biofilm can also entrap metal ions from water solution through a variety of biochemical processes, including enzyme-catalyzed complexation into biological molecules, redox reactions and micro-precipitation (Chakravarty and Banerjee, 2012; Fathollahi et al., 2021).

Accepting the complex frame of Fig. 2c leads to postulating multi-compartment-type uptake kinetics for metals, where the following process take place sequentially: interaction with polypeptides (passive process), possible facilitation of cation permeation by bacteria membrane proteins (active process), and storage in the cytoplasm at the net of elimination processes (Zhang et al., 2021). The significance of this mechanisms for metal ions uptake by biofilms was never studied in the context of accumulation of metal on plastics and represent an important area of developments in the incoming years.

4. Experimental and analytical challenges in the study of plastic-element interaction

The interaction of (trace) elements with MPs has been experimentally investigated employing two different approaches that can be described as top-down and bottom-up. The top-down approach encompasses studies that determined the element concentrations and multiphase distribution in MPs sampled from the environment through chemical extractions or direct surface analysis, whereas the bottom-up approach is embodied by studies aimed to elucidate the mechanisms of plastic-metal ion interaction in controlled (laboratory) or semi-controlled (in-situ) conditions, evaluating the thermodynamics and kinetics processes driving the adsorption of metals.

4.1. Top-down approaches on plastic-water phase distribution assessment of metals

The top-down approaches enable to investigate the likelihood of metal adsorption through the collection and analysis of environmental plastics. The main steps include the collection of samples and the (potential) pre-treatments, which can be followed by extraction/dissolution and analysis of solutions or direct instrumental analysis to investigate the load of adsorbed elements. Each of these steps introduces technical challenges that can confound the measurement of metal distribution. These are described in the following sections with a special focus for studies with MPs.

4.1.1. Collection and sample processing of environmental MPs

Sampling collection and pre-treatment processes play a major role for quality and reliability of measurements. Accordingly, several reviews have been devoted to this topic, covering marine waters (Prata et al., 2019), freshwaters (Campanale et al., 2020), sediments (Adomat and Grischek, 2021; Bellasi et al., 2021), fish and aquatic invertebrates (Lusher et al., 2017). Sampling from water environments is usually (in

about 70% of the studies) performed by deploying nets of different mesh sizes and collecting MPs from large volumes of water. Alternatively, discrete or continuous sampling of water with in-line filtration is applied (Cutroneo et al., 2020). The large number of procedures and equipment applied to MP sampling and separation is a known concern for data comparability. Density separation is typically performed to isolate plastics from other solids in the samples. This is for example a fundamental step for extracting MPs from sediments. Density separation methods utilize concentrated NaCl, NaI or ZnCl_2 solution (He et al., 2020), which can alter the natural element distribution (Stock et al., 2019; Wang and Wang, 2018). This main issue affecting all MP-related fields inevitably also affects the recent analysis of their interaction with inorganic components.

In elemental analysis, sample dissolution generally consists of dissolving adsorbed species by treating MPs with acids and “presenting” them to an analyzer (typically, Inductively Coupled Plasma mass spectrometry, ICP-MS; Inductively Coupled Plasma Optical Emission Spectroscopy, ICP-OES; or Atomic absorption spectroscopy, AAS). Strong concentrated acid mixtures (e.g., *aqua regia*) are commonly used for this purpose (Brennecke et al., 2016; Holmes et al., 2012; Kutralam-Muniasamy et al., 2021; Li et al., 2020; Maršić-Lučić et al., 2018; Vedolin et al., 2018), often under high temperature and pressure conditions (e.g., microwave-assisted acid digestion; Hildebrandt et al., 2020; Wang et al., 2017; Zon et al., 2018). Such an aggressive process may lead to the partial (or complete) dissolution of the polymeric matrix, thus leading to the extraction of the surface/adsorbed trace elements together with bulk species, which are most likely present as additives in the virgin polymer. For example, metal salts are used in polymer industries as heat stabilizers, metallic stearates have been used as slip agents, while Cd and Pb compounds are used as antioxidants (Hahladakis et al., 2018).

Weakly bonded metals are of higher environmental interest for their environmental implications (Turner et al., 2020). Thus, MP dissolution and the release of bulk species should be differentiated to accurately investigate adsorbed elements that are exchanged with the environment. Extraction/leaching protocols under milder conditions (e.g., diluted and less aggressive reagents, Table 2) are accordingly emerging as a promising alternative to selectively dissolve adsorbed elements while preserving the integrity of MPs and the metal content present in origin in the polymer matrix (F. Gao et al., 2019; Hodson et al., 2017; Smith and Turner, 2020; F. Wang et al., 2019). These studies show that the degree of desorption may strongly vary depending on the nature of the elements and polymer.

Bioavailability of contaminants adsorbed on MPs was evaluated in more detail by performing standardized physiologically based extraction tests (PBETs) using tailored simulants for human (Liao and Yang, 2020; Smith and Turner, 2020) and avian gastric conditions (Holmes et al., 2020; Smith and Turner, 2020; Turner, 2018). Focusing on the former, the migration of metals and metalloids under the conditions reported in the European Toy Safety Directive (HCl 0.07 M for 2 h at 37 °C, Spanu et al., 2021b) was recently proposed as a standard reference limit for mammal ingestion (Smith and Turner, 2020).

Thus, differently from acid digestion protocols, selective leaching may provide effective qualitative indications on the strength and type of MP-element interactions. While significant developments are on-going in this area, there is a clear need for fully validated and generally accepted approaches to metal extraction from environmental plastics. For the future, elemental fractionation protocols (i.e., sequential extraction of differently bonded metals; Hass and Fine, 2010) are expected to play a major role in trace elements-MP analysis. They can concurrently provide a deep characterization of sampled MPs, a comprehension of bonding mechanisms (e.g., physisorbed, strongly bound, etc.) and a risk assessment for bioavailability studies. A good starting point for defining MP specific procedures may be found in fractionation protocols proposed for soil and sediment matrices (Hass and Fine, 2010; Hlavay et al., 2004). Such procedures are at present employed only for detecting changes in elemental fractions in soils after

Table 2

Extraction of metals with mild conditions, including the used reagents, the conditions applied for extractions and the polymer and metal ions tested.

Extraction media	Extraction conditions	Polymer	Extracted species	Reference
HNO ₃ (2%)	Sonication (120 W), 10 min, RT	PP and PVC	Pb, Cu and Cd	(F. Gao et al., 2019)
HNO ₃ (0.1 mol/L)	Sonication (120 W), 10 min, RT	PE	Cd	(F. Wang et al., 2019)
CaCl ₂ (0.01 mol/L)	Flatbed shaker (220 rpm), 2 h, RT	PE	Zn	(Hodson et al., 2017)
Synthetic earthworm guts	Flatbed shaker (220 rpm), 3.5 h, RT	PE	Zn	(Hodson et al., 2017)
NaCl (0.1 mol/L)	Lateral shaking (100 rpm), up to 168 h, 40 °C	PP, PE, PVC, Polycarbonate (PC) + Acrylonitrile butadiene styrene (ABS), PU	Br, Cd, Cr, Hg, Pb and Sb	(Smith and Turner, 2020)
Whole digestive system in-vitro method (WDSM)	1) simulated saliva, under shaken (100 rpm), 5 min, 37 ± 2 °C 2) simulated gastric juice, under shaken (100 rpm), 1 h, 37 ± 2 °C, anaerobic condition 3) simulated duodenal juice + simulated bile, under shaken (100 rpm), 4 h, 37 ± 2 °C, anaerobic condition 4) simulated large intestinal juice, under shaken (100 rpm), 18 h, 37 ± 2 °C, anaerobic condition	PE, PP, PVC, PS and Polylactic Acid (PLA)	Cr	(Liao and Yang, 2020)
CaCl ₂ (0.01 mol/L)	Flatbed shaker (150 rpm), 24 h, 22 ± 2 °C	PE, PP, PVC, PS and PLA	Cr	(Liao and Yang, 2020)
Avian physiologically based extraction test (PBET)	Lateral shaking (100 rpm), up to 168 h, 40 °C	PP, PE, PVC, PC+ABS, PU	Br, Cd, Cr, Hg, Pb and Sb	(Smith and Turner, 2020; Turner, 2018)
Avian PBET	Lateral shaking (100 rpm), up to 168 h, 40 °C	PE	Fe, Mn, Co and Pb	(Holmes et al., 2020)
Dietary adapted PBET	Lateral shaking (100 rpm), up to 168 h, 40 °C	PP, PE, PVC, PC+ABS, PU	Br, Cd, Cr, Hg, Pb and Sb	(Smith and Turner, 2020)
HCl (0.07 mol/L)	Lateral shaking, 2 h, 37 °C	PP, PE, PVC, PC+ABS, PU	Br, Cd, Cr, Hg, Pb and Sb	(Smith and Turner, 2020)

interactions with MPs (Li et al., 2021; Yu et al., 2021, 2020), but were not applied directly to MP particles. Drawing from those experiences a five step sequential extraction protocol is proposed here for application to MPs (Fig. 3), including the following phases: 1) exchangeable species, usually including physisorbed elements; 2) associated to carbonates; 3) associated to oxy/hydroxides of manganese and iron; 4) associated to organic matter; 5) residual. The presence of some of the above mentioned phases is sparsely reported on plastic particles: Mn and Fe oxy/hydroxides and carbonates were described in incubation and laboratory conditions only (see e.g., Kniggendorf et al., 2020; Leiser et al., 2020), whereas organic phases, mainly biofilm, are the subject of a large number of studies (Nielsen and Jahn, 1999; Oberbeckmann and Labrenz, 2020; Rummel et al., 2017).

However, the main challenge in the application of such a fractionation protocol is the low concentration of adsorbed elements in the different phases, making their analysis difficult. To overcome this issue the utilization of a simplified, clean sequential extraction procedure requiring limited amount of extracted sample is recommended (Binda et al., 2018; Ciceri et al., 2008), followed by detection through a high sensitive analyzer such as ICP-MS. In this way, the most abundant trace elements (few to tens of ppm, e.g. Fe, Mn and Zn) may be detected in individual fractions, whereas other metals (below 0.1 ppm, e.g. Cd and Pb) could be analyzed as a bulk after aggregating the individual fractions at levels expectedly close to the detection limits of ICP-MS (Holmes et al., 2012; Maršić-Lučić et al., 2018).

Quantitative data of metal extracted from MPs should be then compared at least with the concentration of (trace) elements present in

the sampled aquatic matrix, in order to calculate distribution coefficients. Furthermore, the analysis of metals in other solid constituents of water or sediments could elucidate the role of plastic in metal speciation throughout different environmental compartments (e.g., Yu et al., 2020). Unfortunately, despite its importance, analysis of water phase is far from being a widely adopted practice when studying metal concentration on plastics collected from the environment (but Carbery et al., 2020; Li et al., 2020).

4.1.2. Instrumental analysis: options and limitations

Besides traditional analysis by ICP-MS on metals extracted from samples, MP-element interactions can also be investigated by direct analysis of metal on the plastic surface. Traditional methods used for analyzing elements on surfaces are employed for this purpose. These are: X-ray photoelectron spectroscopy (Dong et al., 2020; Tang et al., 2021), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX, Prunier et al., 2019) and laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS, El Hadri et al., 2020). The main advantage of these techniques is that no specific pretreatment is required, largely reducing the risk of altering the natural MPs surface during sample preparation and extraction. Quantitative/-semiquantitative information may be gathered by these non-invasive techniques, which, unlike extraction/dissolution methods, analyze specifically element content on the surface of plastics with a probe depth ranging from ~5 nm (using XPS) to 1–2 µm (using SEM-EDX). This approach fits the purpose of examining specifically the interactions at the MP-environment interface, solving the problem of the possible

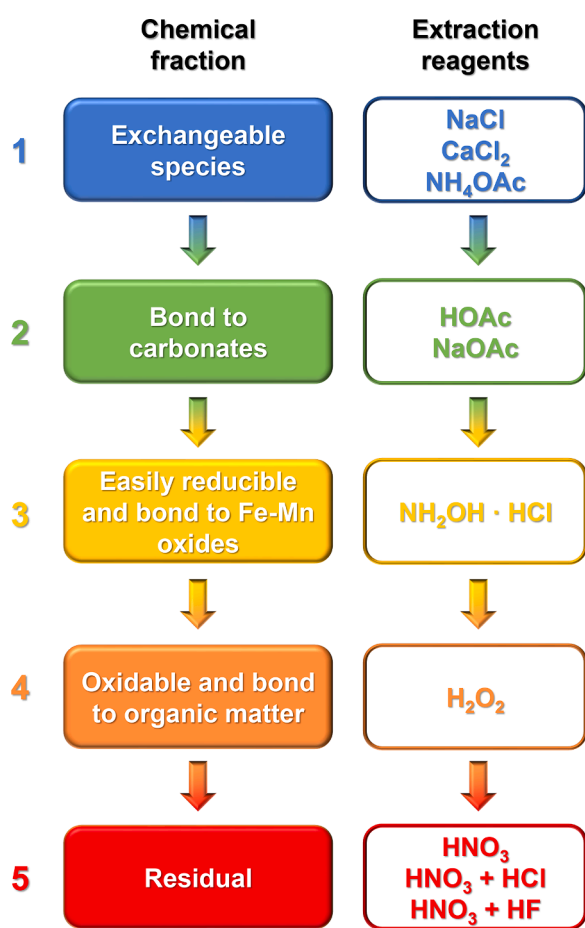


Fig. 3. Sketch of a typical extraction scheme for different phases of metals bonded to solid particles (soils and sediments), which can possibly be applied to environmentally collected MPs. The typical analyzed phases and the most commonly used extraction reagents are listed for the different sequential steps.

undesired extraction of metals possibly present in the polymer matrix at source together with the metals acquired from the environment. Furthermore, XPS can be useful for preliminary qualitative MP characterization providing fundamental information on the chemical composition and state of the MP surface (e.g., the presence of O- and N-containing surface functional groups which can play a key role in the adsorption process). As a drawback, the low sensitivity of XPS and SEM-EDX makes them suitable for the determination of minor and major elements, but not of trace elements: detection limits down to 0.1 and 0.01 atomic percent are reported for SEM-EDX and XPS, respectively (Nasrazadani and Hassani, 2016; Shard, 2014). Reliable trace element quantification can instead be achieved by LA-ICP-MS thanks to the much higher sensitivity (Monticelli et al., 2018), even in polymeric materials (Spanu et al., 2021a). LA-ICP-MS can discriminate between bulk and surface species by determining concentration depth profiles (surface to bulk), as demonstrated by El Hadri et al. (2020).

XPS may be an effective tool to perform speciation analysis for a more detailed assessment of plastic-elements interaction. It should be applied not only for the identification of MP surface functional groups (as normally done) but also for the speciation of adsorbed species, which would provide new insights for formulating and assessing mechanistic hypothesis regarding the adsorption process. At present, such approach was applied only for As species adsorbed onto PS (Dong et al., 2020). Hence there is a highway for future exploitation of this techniques in this research area. Furthermore, XPS can be employed to perform depth profiling analysis with a nanometric depth resolution. This approach may disclose new opportunities to gather insights on the diffusion of

inorganic contaminants through the very first atomic layers of plastics. Finally, XPS analysis can be used specifically to assess metal contents in the biofilm covering the MPs. This appears to be an excellent opportunity to gather experimental evidences of the possible pivotal role of biofilms in determining uptake of metal by plastics in the environment.

Secondary Ion Mass Spectrometry (SIMS) is another surface analytical technique that shows very high sensitivity, suitable for trace element quantification, mapping, and depth profiling. To date, SIMS has been used limitedly for the evaluation of the degradation of plastic debris by looking at changes in the mass spectral pattern of the polymer as well as to identify and visualize (imaging) microplastic particles in complex matrices (Biesinger et al., 2011; Du et al., 2020; Jungnickel et al., 2016). Only very recently a SIMS-based technique (time-of-flight SIMS, ToF-SIMS) has been applied for the first time to study the interactions between plastics and metals to study the diffusion of Cu²⁺ and Ni²⁺ ions into PP (Fig. 4, Kern et al., 2021).

4.2. Bottom-up approaches

Here we describe and critically review approaches adopted for characterizing trace element – MP interactions under controlled (laboratory or field) conditions. These studies generally aim at determining the thermodynamics or the kinetics of trace element adsorption onto MP surfaces (see Section 3.1). Thermodynamic investigations (Godoy et al., 2019; Guan et al., 2020; Zou et al., 2020), kinetic studies (Aghilinasrollahabadi et al., 2020; Brennecke et al., 2016; Fernández et al., 2020; Lin et al., 2021; Tang et al., 2021) or both (Davranche et al., 2019; Dong et al., 2020; Xuan Guo et al., 2020; Holmes et al., 2014, 2012; Lang et al., 2020; Oz et al., 2019; Tang et al., 2020; Turner and Holmes, 2015; F. Wang et al., 2019; Wang et al., 2021; Zhou et al., 2020; Zon et al., 2018) were performed on MPs sampled from the environment (Holmes et al., 2012; Tang et al., 2021), pristine polymers (Godoy et al., 2019; Zou et al., 2020) and artificially aged polymers (Aghilinasrollahabadi et al., 2020; Lang et al., 2020).

4.2.1. Critical issues in currently applied methods

As already stated in Section 3.1, the controllable conditions of simulation methods make isotherms and kinetics experiments the ideal candidates for modelling studies on MP-element interactions. However, the absence of harmonized/standardized procedures for boundary conditions (i.e., the actual environmental conditions during adsorption experiments and the aging process of MPs) often hinders comparability among existing data (see Table S1 in Supplementary Material). Several critical aspects should be addressed for ensuring experiments yield reliable and environmentally relevant data. First, times play a role when adsorption isotherms are measured. Enough time should be allowed for the system to reach equilibrium, hence studies that focus on equilibrium should be complemented with kinetic experiments aimed at evaluating a valid experimental timeframe. Available studies have used timeframe ranging from 4 h (Davranche et al., 2019) to two weeks (Godoy et al., 2019), with typical values of 24–48 h. It should be also considered that the equilibration time can vary for the different active sites of plastic particle: different mechanisms are at work for plastic-element interactions (Y. Wang et al., 2020) and may require different times to reach equilibrium. The latter point is also clearly environmentally relevant, as the residence time of MPs and trace elements varies widely in the environment, limiting or extending the kinetically accessible processes. As an example, only fast processes may be active in a highly dynamic environment like an estuary, whereas months may be allowed for interactions to occur in soils.

Another critical issue is the scarce representativeness of natural conditions given by the solution phase used during equilibrium and kinetic experiments. Generally, the adsorption of single (or few) trace elements onto artificially aged MPs is performed under extremely simplified conditions (e.g., distilled water or salty solutions at controlled pH). This minimalistic set up is not representative of natural water

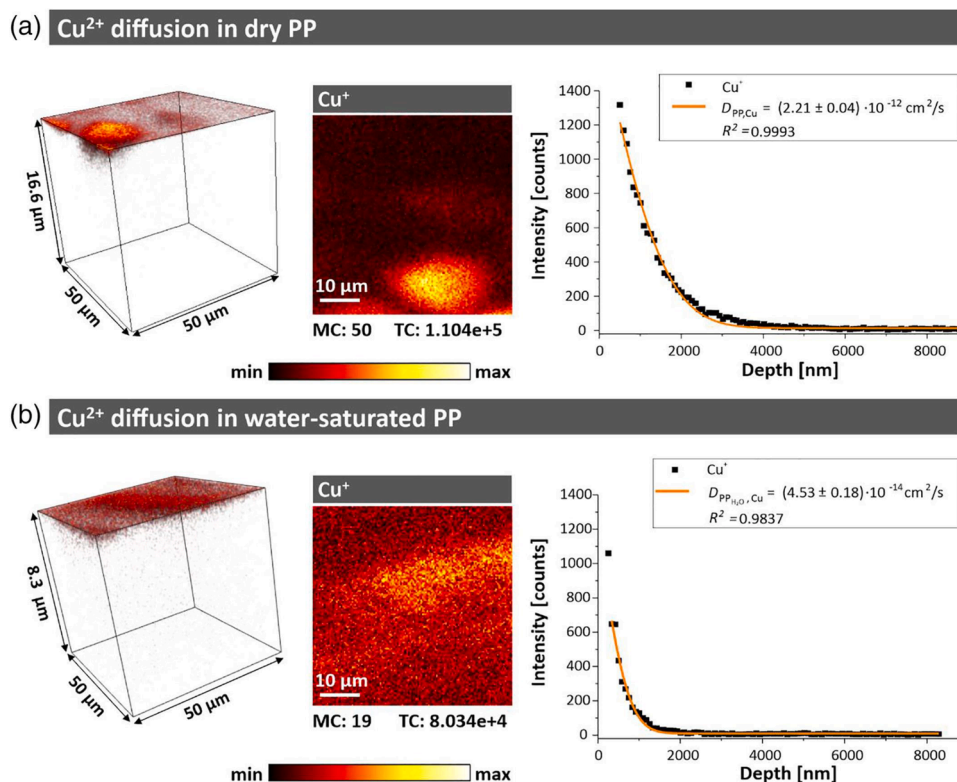


Fig. 4. Example of a first application of ToF-SIMS on metal adsorbed on plastic. (a) Diffusion of Cu^{2+} in PP with a residence time for Cu^{2+} of 1 hr. (b) Diffusion of Cu^{2+} in water-saturated PP with a residence time of Cu^{2+} of 1 hr. For both panels, left: 3D mass spectrometry data shows Cu^{2+} diffusion into polymer; middle: 2D mass images. Right: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiles (image reprinted from Kern et al., 2021; under creative common license).

matrices. While synthesis and simplification is pivotal when designing experiments, studies with more realistic conditions (e.g. use of environmentally relevant pH conditions and ion concentrations, co-presence of ligands and dissolved organic matter in the solution) should be considered too, in order to enable a sound extrapolation of findings from minimalistic experiments to real environmental conditions. To this regard, it is noted that all laboratory studies used very high concentrations of trace element (usually in the milligram per liter range, with few study using concentrations down to tens of microgram per liter; Davranche et al., 2019; Guan et al., 2020; Holmes et al., 2014, 2012). These concentrations (even the lowest ones) occur in the environment only in extreme conditions, like mine waters or anoxic water in peculiar geological settings (e.g., Binda et al., 2020; Rahman et al., 2021) and are never met in seawater or freshwater bodies. Similar problems are observable for pH. Acidic pH values are often used in combination with high element concentrations to hinder element precipitation as oxo/hydroxides (Oz et al., 2019; Tang et al., 2020), providing unrealistic conditions to describe typical environmental settings.

Only a limited number of studies considered the competition by dissolved organic matter (Tang et al., 2021; Wang et al., 2021; Zhou et al., 2020) or suspended particles (Guan et al., 2020). This lack of focus on the role of organic ligands in strident conflict to the well-known behavior of trace elements that are typically almost completely complexed to these compounds in both freshwater (Monticelli and Caprara, 2015) and seawater (Y. Gao et al., 2019).

The exploration of MP-metal ion interactions at such high metal concentrations in acidic conditions may lead to an unrealistic picture of the interaction mechanisms and dynamics occurring in environmental settings. In particular, molecular sites with different binding affinity and concentration are likely to be present on MP surfaces (Xuan Guo et al., 2020), meaning that unrealistically high exposure levels may blur or completely hide the potentially important role of binding sites with high

affinity but low density in the plastic surface (the heterogeneity of binding sites is well described for complexing species in natural waters in Filella and Town, 2003). Considering the trace or even ultra-trace element levels in natural waters, these undetected sites may well be the only sites involved in trace element-MP interaction under environmental conditions.

During laboratory experiments other factors may influence dissolved concentrations of metals and hence possibly affect the experiment outcomes. For example, adsorption onto container walls and precipitation can easily happen, resulting in a removal of the elements from the solution phase that is uncorrelated to the sorption onto plastics. These phenomena may be easily assessed by including adequate experimental blanks. While this may seem obvious, blanks have been mentioned only in one of available studies, yet without reporting blank results in the paper. Moreover, conditioning of the container used for the experiments should be performed to avoid “wall effects” (see e.g., Sanvito and Monticelli, 2021). Such a procedure is usually adopted in available studies, but the glassware is conditioned only with the solution before adding the elements. Solutions containing at varying concentrations should be instead added in the containers and left for enough time to reach equilibrium, and then containers should be rinsed with distilled water. This procedure should be performed at least twice before proceeding with the adsorption experiments.

Finally, the MP molecular, micro/macroscopic characteristics and aging level should be carefully evaluated and described to enable comparison of results across different studies. For example, concerning ageing, different types of environmental stresses are described to simulate weathering of MPs, however work focuses so far mainly on the effect of a single or a limited number of factors, which mainly include surface oxidation (chemically or UV-induced). In this way, only the effect of single features of aged MPs (e.g., specific surface area, surface functional groups, biofilm formation) on the interaction with metals

may be currently gained. As already stated in Section 2, the effective reproduction of natural ageing process is needed for a realistic simulation of MP-element interaction, which should in particular account also for biological processes.

4.2.2. Recommendations for future experimental works

Following the options and limitations described in this chapter, it is recommended that adsorption isotherms and kinetic experiments should:

- 1 Use environmentally relevant conditions in terms of trace element concentrations (no more than 10 times the environmental ones), pH values and major element composition.
- 2 Evaluate time for equilibrium prior to experiment.
- 3 Include the necessary blanks to assess possible experimental interferences and/or artifact (e.g., evaluate the set up without addition of MPs to assess glassware effects or any reactivity in the solution phase or without the addition of metal ions, to evaluate any possible leaching of metal already present in the plastic specimens).
- 4 Use high sensitivity/high resolution analytical techniques (typically ICP-MS) to enable the detection of trace and ultra-trace levels of elements.
- 5 Evaluate adsorption kinetics in accordance with the residence times of MPs and trace elements in the environmental compartments.
- 6 Use of combined and harmonized aging methods, attempting to faithfully reproduce environmentally aged MPs.

After following these basic recommendations future experiments could be designed in a variety of different ways to move forward knowledge of MP-element interactions. For example, a detailed mass-budget approach is strongly envisaged whereby trace element masses are analyzed in both the solution, the MPs and the glassware surface at the end of the experiments and compared with the total mass added in the system at the beginning of the experiment. This would enable controlling for possible confounding effects driven, for example, by leaching of metals native in the plastic specimens.

Moreover, and importantly, element speciation should be included in the experiments (Pesavento et al., 2009). Species differing in redox state (Cr(III) and Cr(VI)), complexation (elements bound to or adsorbed onto natural organic matter), organic and inorganic ligands (inorganic and organic mercury species like methylmercury) are expected to interact differently with MPs surfaces. Up to now, the behavior of Cr(VI) only has been selectively investigated (Turner and Holmes, 2015).

As a final remark, the combination of these bottom-up approaches with the abovementioned top-down approaches based on field observations (Section 4.1) represent a suitable way to complete the understanding on the mechanisms MP-elements interactions. Experimental procedures such as sequential extraction procedures are likely to provide information on the kind of interactions that are at work in the environment. In this way, a more detailed knowledge on the occurring adsorption in real environmental conditions can help in modulating at best the water and plastic-related parameters for experiments in controlled batches.

5. Conclusions and perspectives

This review highlights the recent and increasing research interest on the interaction of plastic with metals, as an emerging research avenue in the plastic pollution area. Considering the still early stage of development, several limitations and gaps need to be addressed before a satisfactory comprehension of the mechanisms underlying plastic-metal ion interaction can be achieved. While early experimental works have shown that (trace) elements interact with plastics essentially through weak surface interactions, the molecular domains on plastic surfaces responsible for the interaction are still poorly understood. Similarly, the role of water-side composition (e.g., the presence of ligands, ions and

other compounds competing for binding sites, co-occurring and interacting with metals in the solution phase) and properties (e.g., pH, redox potential) is unclear. While studies have so far privileged a reductionistic approach focusing on simplified experimental setups, the adoption of a more holistic (yet detailed) conceptual frame (such as the one described in Fig. 2), describing the system through its progressive levels of complexity (fundamentally determined by the level and typology of plastic ageing), can help directing future and more detailed research. In particular, the role of biofilms should be carefully considered in future studies. Background knowledge suggests in fact that microbiota forming biofilms possess dedicated structures and physiological processes enabling them to actively uptake metal ions as micronutrients. Hence, biofilms may have a pivotal contribution to the core capacity of plastics for accumulating metals, that has so far been overlooked.

Furthermore, there is a demand to design sorption/desorption experiment with a more realistic and well-defined selection of conditions (e.g., using realistic trace concentrations of metals, water physicochemical conditions varying in the environmental range, plastic specimens fully characterized for their chemical and/or biological ageing). This will ensure more representative and intercomparable results.

Along with laboratory-based research, the analysis of environmental samples and the study of fractionation of elements adsorbed onto MP particles will contribute to shed light on the adsorption mechanisms relevant for the environmental context.

Finally, future studies should focus with more detail on the water-side, assessing the effective adsorption/desorption also of major elements dissolved in water (e.g., N, P, Ca, K). These can in fact potentially interact with environmental plastics similarly to trace elements, especially if the adsorption mechanisms are non-selective. Translating knowledge gained on plastic-metal ion interaction to the interaction with other ions serving as macronutrients can be key for understanding the broader indirect impacts of plastic pollutions on water ecosystems (e.g., alteration of cycling of elements, Seeley et al., 2020).

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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Supplementary materials

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