

A MINI-REVIEW ON THE MICROPLASTIC-HEAVY METAL INTERACTIONS AND THE FACTORS AFFECTING THEIR FATE IN AQUATIC HABITATS

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ABSTRACT Microplastic particles found in water bodies are recognized a serious environmental concern due to their effects on aquatic biota. Microplastics, with their large surface area, are considered as vectors since they provide suitable surfaces for the adherence of several toxic pollutants, including heavy metals, pesticides, and nanoparticles. Several physico-chemical properties of plastic particles including chemical structure, polymer chain organization, specific surface area, and particle dimensions, and environmental parameters (ambient temperature, pH and salinity of the media and the dissolved organic matter concentration) may reshape the dynamic interactions between heavy metal ions and microplastic surfaces. Microplastic-heavy metal interaction poses a global health threat to aquatic biota and eventually human beings through the food chain since attached metal ions may be transported to aquatic organisms. Therefore, it is critical to clarify the mechanisms responsible for the adherence of metal ions to plastic surfaces. Such an approach will help government departments to promote management strategies and design of treatment practices. In this study, recent reports on the adherence of heavy metal ions to microplastic particles in aquatic habitats, along with the factors that might change the adsorption capacity of microplastics, are reviewed and discussed in detail.

Keywords Pollution, heavy metal, microplastics, adsorption

1. INTRODUCTION

The family Brassicaceae is represented by 321 genera in the world [1] and 96 genera in Türkiye [2]. The genus *Barbarea* is represented by 29 species in the world [3] and 19 taxa belonging to 14 species in Türkiye, 11 of which are endemic [4, 5]. Members of this genus are distributed in the warm regions of Eurasia, Australia, and North America, and in some countries of South America and the eastern parts of Africa. Plastics are strong and light, resistant to water and shock, poor conductors of electricity and heat, and are highly flexible and durable [1]. Furthermore, they can be produced in great masses with low costs [2]. Thus, they are widely favored in packaging, textile, construction, transportation, electronics and automotive industries and in the production of several household goods [3, 4]. Manufacture of several household and industrial plastic goods has increased steadily on a global scale since 1950's and increased

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approximately to 391 million tons in 2021 on a global basis. Furthermore, the estimates reveal that it will reach 33 billion tons by 2050 [5, 6]. The abundance of plastic wastes discharged into environment increased over the last years because of increasing the global demand to plastic materials [7, 8]. Plastic materials constitute 54% of the wastes in nature by mass [4, 9]. Although, there is a great effort to enhance reuse rate of plastic wastes, estimations reveal that only less than 10% of plastic products could be recycled globally [4]. Aquatic habitats function as an environmental sink for several hazardous chemicals such as heavy metals [10], pesticides [11], nanoparticles [12] and plastics [13] released into the environment. Approximately up to 13.10^6 tons of plastic debris are drifted annually from land-based habitats to oceans [14]. Plastic wastes are non-biodegradable. For example, it takes 500 years for a bottle made of high-density polyethylene (HDPE) to degrade completely in soil [15], or quite longer for some other plastic goods such as monofilament fishing line in the marine habitats [16]. Therefore, plastic waste accumulation increases gradually in aquatic habitats [17].

The particle size of plastic waste material released into terrestrial and aquatic ecosystems range from micrometers to meters. Microplastics particles range between 1 μm to 5 mm in diameters [13, 18] which are further divided into 2 categories; primary and secondary particles. The former is directly produced for industrial use such as medical, textile and cosmetics [19, 20]. Secondary microplastic particles originate from the bigger plastic materials which break into fine particles through physical, chemical and biological processes [21, 22]. Microplastics can be found in various shapes including pellets, particle fiber, films, beads, and foam based on the appearance of particles [23, 24]. Their color shows great variability including yellow, cream, white, transparent, orange, blue, purple, green, and opaque [25]. Although, polyethylene is the prevalent man-made polymer type, several other polymer types are also available; polyvinyl chloride (PVC), polyamide (PA), polyethylene terephthalate (PET), polypropylene (PP) and polystyrene (PS) [26].

The prevalence of plastic particles in the seas has increased remarkably soon after their first record in 1970s [27]. For instance, the Northwest Pacific Ocean's surface water contains up to 42,000 units/ km^2 of microplastics [28]. Estimations affirm that 80% of land-based plastic wastes are disposed into oceans either directly from wastewater treatment facilities or indirectly through rivers and surface runoffs [29,30]. Microplastics can move great distances within the atmosphere by wind, storm, hail, and precipitation [31, 32]. Microplastic particles are observed even in highly isolated regions on earth including the Arctic Ocean, isolated ocean islands, and even deep ocean waters [33]. In a recent survey, the amount of the microplastic particles in the Arctic Sea (depth ~16 cm) were found as 0-1.31 particles/ m^3 [34].

Microplastic particles found in atmosphere, terrestrial and aquatic habitats create a global health concern for several organisms and eventually human beings through consumption of contaminated food items and can be accumulated in the body of several aquatic animals [35-39]. Biochemical, physiological and

behavioral alterations [13, 40] including genotoxicity [41], oxidative stress [21], abnormalities in glycolipid and energy metabolism, disturbance of inflammatory response [42] and death [43] are reported in several aquatic animals after exposure to microplastic particles.

Microplastics may contain various amounts of toxic compounds and endocrine disruptors such as bisphenol A, triclosan, bromine based flame retardants, dyes, pigments, and biphenyl in their chemical structure [44, 45]. Due to their interactions with other toxic compounds, particularly heavy metals (HMs) in aquatic environments, they are referred as vectors [46] or more commonly a Trojan horse [33]. Adsorption of contaminants present in aquatic environments to microplastic surfaces can increase retention time of that contaminants in the pelagic zone [47, 48] and causes the organism to be exposed to a greater concentration when ingested [39, 49, 50].

Heavy metals, generally defined as metal and metalloid groups with densities exceeding 5 g/cm³, pose a significant threat to organisms due to their potential toxicity and ecotoxicological effects [10, 51]. Heavy metals typically exist as sulfates, hydroxides, oxides, phosphates, and silicates in the Earth's crust [52, 53]. Despite their detrimental nature, these elements are ubiquitous in the environment, released through both natural processes (forest fires, rock weathering, volcanic activity, erosion, etc.) and anthropogenic activities (agriculture, mining, industry, etc.) [54]. These elements have several uses across numerous sectors due to their unique properties, including conductivity, catalytic activity, high density, corrosion resistance, magnetism, biocidal activity, and their ability to form versatile alloys [55]. Some of the heavy metals are considered as essential such as iron, copper, cobalt, zinc, chromium, molybdenum, selenium, and manganese. Although essential heavy metals are critical micronutrients for physiological and biological functions and required at moderate or trace amounts, excess levels can trigger adverse effects. For example, copper is essential for a variety of biological functions and is used as a cofactor in many enzymes [56]. But, high levels of copper can lead to Alzheimer's disease, gastrointestinal disorders, and organ damage [57, 58]. On the other hand, some of the heavy metals such as aluminum, antimony, arsenic, barium, beryllium, cadmium, mercury, and lead pose a significant threat to organisms even at quite low concentrations and considered non-essential heavy metals [59]. Their toxic effects are documented in numerous studies, affecting vital organelles like the cell membrane, mitochondria, and nucleus, disrupting DNA, cell cycle, and inducing carcinogenesis and apoptosis [60]. Furthermore, their concentrations are increasing exponentially within the food web due to their persistence and bioaccumulative nature [53]. Thus, there is a great concern on their toxic effects on organisms from an ecological standpoint. Each heavy metal has its own unique physical and chemical characteristics [61]. In addition, their interactions with other elements, toxicity to organisms, deposition, presence in water column, uptake and accumulation in cells are dependent upon several abiotic and biotic parameters. Thus, as mentioned above the presence of

microplastic particles (MPs) creating a suitable surface for adherence of heavy metals may increase their uptake (either voluntarily or involuntarily ingestion of MPs) by living organisms and the residence of heavy metal ions in the water column [46].

For example, Ashton et al. [62] reported that new polyethylene pellets strongly adsorbed the manganese (Mn), lead (Pb), aluminum (Al), cobalt (Co), silver (Ag), iron (Fe), tin (Sn), copper (Cu), zinc (Zn) and molybdenum (Mo) ions when exposed to seawater for eight weeks, in Sutton Harbor. Similarly, adsorption of mercury (Hg) to microplastic particles in marine environment increased when exposed to metal ions for longer periods [63]. Microplastic particles initially have a non-porous structure but undergo significant surface transformations due to weathering, abrasion, and photo-oxidation in aquatic environments. These processes not only enhance their adsorption potential by increasing specific surface area, but also generate negatively charged sites in natural aqueous environments [64]. Consequently, these negatively charged microplastic particles act as potent adsorbents for positively charged heavy metal (HM) ions through electrostatic interactions which is the primary driver of adsorption. In addition, Van der Waals and π - π interactions which are specific to certain polymer type play a complementary role [65]. Furthermore, biofilm and dissolved organic matter mediate the complexation and accumulation of heavy metals on microplastic particles through altering the surface properties. Thus, adsorption of HMs to MPs are enhanced through presence of organic molecule interactions, increased charge, roughness, porosity, and hydrophilicity [64,66]. However, there is a debate on the adsorption dynamics of heavy metal ions to microplastic surfaces. Several factors including chemical composition, polymer chain organization, specific surface area and dimensions of the particles and environmental factors (temperature, salinity, dissolved organic matter, pH, etc.) and treatment methods applied (ball milling, UV radiation, Fenton and hydrogen peroxide aging, etc.) have been found to affect adsorptive capacity of microplastic particles for heavy metal ions [67-71]. The ecological risks associated with heavy metal contamination, are increased by the interaction between microplastic particles and HM ions. Therefore, it is vital to reveal the complex adsorption mechanisms from an environmental standpoint, in order to plan management strategies and design treatment practices. In this study, recent reports on the adherence of HM ions to microplastic particles in aquatic habitats, along with the parameters that might alter the adsorption dynamics, are reviewed and discussed in detail.

Microplastic-Heavy Metal Interactions in Aquatic Habitats

During recent years, the threat raised by the interaction between microplastic particles and HMs in aquatic habitats gained attention from scientists worldwide [72]. The concentration of HM ions adsorbed to microplastic surfaces can be quite higher compared to the HM ion concentration in the aquatic media (Table 1). For example, HM load in the Beijang River sediments were considerably less than the HMs adsorbed by microplastic particles [73]. Likewise, Liu et al. [74]

compared HM ion concentration and microplastics in water samples collected in Hong Kong from 5 meters below the water's surface. They found that Pb^{2+} ion concentration absorbed by microplastics ranged from 0.72-1.742 $\mu\text{g/g}$, whereas the total Pb concentration in sea water was ranging between 0.09 and 0.51 $\mu\text{g/L}$. We summarized the data available on the sorption of HM ions to microplastic particles in aquatic environments in Table 1.

Factors Effecting the Microplastic Adsorption Capacities

To accomplish a better insight on the adsorption kinetics of HM ions to plastic particles, simulations were carried out under fully controlled laboratory studies. Table 2 summarizes the adsorption capacity and the factors affecting the adsorptive capacity of common plastic polymers observed in aquatic environments for several heavy metals. In the studies summarized, selected and known amounts of microplastics and HM ions were added to the experimental media and the adsorbed heavy metal concentration was measured after certain periods of time. In general, the physico-chemical properties of microplastics (chemical structure, specific surface area, particle dimensions and polymer chain organization), laboratory simulation methods and environmental factors (dissolved organic matter concentration, ambient temperature, salinity and pH of the media) are shown to have a great effect the adsorption dynamics [68, 87, 88]. Several researchers tried to imitate the environmental weathering of plastic particles by aging them through ball milling, oxidation and UV radiation. Their results confirm that heavy metal ion adsorption rates increase as the particles age [89-91]. Researchers attributed this situation to the alteration of the surface features of particles after mechanical abrasion or oxidation [92]. For instance, the concentration of arsenic ions adsorbed to polystyrene microplastic particles (PSMPs) increased after ball milling which increased the SSA of particles [91]; they also found that arsenic ion concentration adsorbed to particles decreased with increasing PSMP size. Similarly, the Cd^{2+} adsorption ability of microplastic particles exposed to Fenton and H_2O_2 solutions, were found to increase with increasing aging time [69]; they also found that Fenton was a better aging agent compared to H_2O_2 . PET particles aged by exposing to UV radiation was also found to have a greater adsorption efficiency with increasing exposure time; therefore, indicating that microplastics exposed to sunlight can adsorb larger amounts of heavy metals [68].

TABLE 1. The comparison of heavy metal concentrations in water and sediment samples and the heavy metal concentration adsorbed to microplastics in aquatic habitats.

Location	Sampled compartment	Sampling Method	Analysis Method	Concentration of microplastic particles	Polymer type	Heavy Metal concentration in water	Heavy metal concentration adsorbed to microplastics	References
Plymouth and Kingsbride Estuary, England	Beach	Plastic tweezers	Ultrasonication (5 min) Washed in aqua regia SEM-EDS FT-IR ICP-OES ICP-MS	100 particles/m ²	PE plastic pellet	Al: 6.20±3.65 µg/g Fe: 17.98±7.49 µg/g Mn: 2.61±1.97 µg/g Cu: 0.28±0.18 µg/g Pb: 1.72±0.92 µg/g Zn: 0.25±0.18 µg/g Ag: 24.7±9.4 µg/g (heavy metal concentration on new polyethylene pellets suspended in harbor for 8 weeks)	Al: 7.05±0.66 µg/g Fe: 25.85±2.09 µg/g Mn: 1.58±0.57 µg/g Cu: 0.06±0.03 µg/g Pb: 0.15±0.04 µg/g Zn: 0.55±0.27 µg/g Ag: 2.4±0.4 µg/g (heavy metal concentration in pellets collected from the beach)	[62]
Musi River, Indonesia	Surface water	Neuston net (300 µm)	Suspended in NaCl (1.2 g/cm ³) Washed in 95-97% H ₂ SO ₄ and HNO ₃ Stereomicroscope ATR-FT-IR AAS	-	PES, PP, PE, PVC, Nylon	Pb: 0.0245-0.0711 mg/L Cu: 0.0099- 0.0173 mg/L	Pb: 0.152-2218 µg/g Cu: 0.012-0.365 µg/g	[72]

Chao Phraya River, Thailand	Surface water	Manta trawl	Organic material was removed with H ₂ O ₂ (%30) and NaI (1.5 g/cm ³) Washed in aqua regia Optic Microscope, Fluorescence Microscope FT-IR μ-FT-IR ICP-OES	80±65 items/m ³	PP, PE, PS	Pb: 0.01±0.00 μg/L Cr: 1.1±0.00 μg/L Cu: 0.05±0.03 μg/L Ni: 0.05±0.06 μg/L	Pb: 17.61±18.26 μg/g Cr: 2.95±2.96 μg/g Cu: 13.02±18.26 μg/g Ni: 0.78±1.11 μg/g	[75]
Freshwater Wetlands, India	Surface water	Steel bucket, Mesh sieve (63 μm)	Density separation method with ZnCl ₂ (1.80 g/cm ³) Organic matter was removed with H ₂ O ₂ (%30) and %1 HNO ₃ Optic Microscope Fluorescence Microscope ATR-FT-IR ICP-MS	7.87-20.39 items/L	PE, PET	As: 0.02-0.24 μg/L Cd: 0.15-1.23 μg/L Cr: 0.85-23.65 μg/L Cu: 0.26-23.14 μg/L Ni: 1.24-42.36 μg/L Pb: 1.24-12.15 μg/L Zn: 15.36-286.35 μg/L	As: 1.56-4.51 μg/g Cd: 0.65-5.78 μg/g Cr: 26.26-342.28 μg/g Cu: 0.29-119.59 μg/g Ni: 12.43-75.77 μg/g Pb: 0.04-104.63 μg/g Zn: 1.88-1191.52 μg/g	[76]
Punnakayal Estuary, India	Surface water	Teflon pump, Stainless steel sieve	Organic matter was removed H ₂ O ₂ (%30) Ultrasonication with %2 HNO ₃ Stereomicroscope μ-ATR-FT-IR AFM ICP-OES	7.8 particles/L	PP, PA, PE, PVC, P	As: 20.56 μg/g Pb: 6.26 μg/g Cd: 6.26 μg/g Mn: 9.37 μg/g Cu: 1.02 μg/g Cr: 0.33 μg/g Zn: 16.24 μg/g	As: 0.12-0.96 μg/g Pb: 4.13-4.56 μg/g Cd: 0.24-0.32 μg/g Mn: 8.59-12.35 μg/g Cu: 0.24-6.33 μg/g Cr: 0-0.24 μg/g Zn: 1.24-5.69 μg/g	[77]

Hong Kong, China	Samples of seawater were collected 5 meters below the sea surface.	Manta trawl (330 µm), Stainless steel sieve	Density separation with NaCl Ultrasonication with %2 HNO ₃ and H ₂ O ₂ (%30) Stereomicroscope SEM ATR-FT-IR ICP-MS	-	PE, PP, PS	Cd: - As: 3.02-3.83 µg/L Zn: 3.79 µg/L Pb: 0.09-0.51 µg/L Mn: 1.03-11.9 µg/L Ni: 0.94-1.39 µg/L Cu: 2.38-4.65 µg/L	Cd: 676 µg/g As: 0.027-28.1 µg/g Zn: 9.58-1.712 µg/g Pb: 0.72-1.742 µg/g Mn: 0.03-248 µg/g Ni: 0.61-34.8 µg/g Cu: 1.22-124 µg/g	[78]
Trombol Beach, Malaysia	Plastic debris	Sampling quadrat	Rinsed under running warm water Washed in 95-97% H ₂ SO ₄ , and %65 HNO ₃ ICP-OES	30 items	PE, PP, PS, PET	-	Cd: 0.3584±1.6 ppm Pb: 1.2696±4.6 ppm Ni: 0.0408±0.3 ppm Cu: 3.3165±8.3 ppm Zn: 4.5515±9.8 ppm As: 0.0193±0.2 ppm Hg: 0.0004±0.0 ppm	[78]
Lake Garda, Italy	Sediment	20 m transect with 10 sediment cores	Density separation with ZnCl ₂ (1.6-1.7 kg/L) Organic matter was removed with H ₂ O ₂ (%30), HNO ₃ (%65) and H ₂ SO ₄ (%95) Raman microspectroscopy ICP-MS	561 particles/m ²	PE, PA, PET, PS, PVC	-	Cd: 23.64 µg/g Cr: 154.23 µg/g Cu: 19.56 µg/g Ni: 1.12 µg/g Pb: 219.7 µg/g Ti: 1046.01 µg/g	[79]

Beijang River, China	Sediment	Stainless Steel Shovel	Density separation with NaCl Ultrasonication (5 min) with H ₂ O ₂ (%30), HNO ₃ (%65-68), and H ₂ SO ₄ (%95-98) SEM-EDS μ-FT-IR ICP-MS	78±69 544±107 items/kg	-	PP, PE	Cd: 0.07±0.01 μg/g Pb: 2.458±0.019 μg/g Cu: 57.93±4.32 μg/g Ni: - Zn: 79.5±2.5 μg/g	Cd: 2.16-17.56 μg/g Pb: 38.24-13.11 μg/g Cu: 80.9-500.6 μg/g Ni: 0.54-2.39 μg/g Zn: 2414-14815 μg/g	[73]
Adriatic Sea, Croatia	Sediment	Stainless Steel Spoon	MQ water Organic matter was removed with HCl (%37) and HNO ₃ (%65) AAS	6-36 particles/dm ³	-	-	-	Cu: 0.08-0.61 μg/g Mn: 0.19-8.25 μg/g Ni: 0.04-0.27 μg/g Pb: 0.04-0.85 μg/g Fe: 18.2-88.5 μg/g Cr: 0.03-0.14 μg/g	[80]
Persian Gulf, Iran	Sediment	-	Density separation with 360 g/L NaCl Washed in aqua regia Epifluorescence microscope ICP-OES	82.612 items/m ²	-	-	Cd: 0.81 ± 0.18 μg/g Cr: 5.01 ± 0.73 μg/g Fe: 3045 ± 11.31 μg/g Al: 186 ± 2.82 μg/g Mn: 126.5 ± 3.53 μg/g Ni: 14.5 ± 0.7 μg/g Pb: 48.55 ± 10.81 μg/g Cu: 5.43 ± 0.73 μg/g	Cd: 0.035±0.007 μg/g Cr: 0.915±0.03 μg/g Fe: 531±135.7 μg/g Al: 114.56 ± 5.47 μg/g Mn: 32.2±12.4 μg/g Ni: 2.03±0.16 μg/g Pb: 4.59±0.53 μg/g Cu: 3.6±0.28 μg/g	[81]
Coast of São Paulo, Brazil	Sediment	Samples were collected by hand	Organic matter was removed with H ₂ O ₂ (%30), pure HNO ₃ and HCl ICP-OES	300 items pellet	-	PP, PE	-	Al: 45±9 μg/g Zn: 8±9 μg/g Cu: 1 ± 1 μg/g Fe: 228±142 μg/g Mn: 9±6 μg/g	[82]

Coast of Hong Kong, China	Sediment	Stainless Steel Shovel and Sieve	Washed in aqua regia ATR-FT-IR ICP-OES	-	PE, PP, PS	Fe: 799±507 µg/g Mn: 25.3±14.6 µg/g Ni: 0.18±0.14 µg/g Cu: 3.47±2.83 µg/g Zn: 24.2±9.29 µg/g	Fe: 302±224 µg/g Mn: 18.6±12.7 µg/g Ni: 0.15±0.13 µg/g Cu: 0.89±0.89 µg/g Zn: 19.6±11.4 µg/g	[83]
Jinjiang Estuary, China	Sediment	Stainless Steel Shovel	Density separation with NaCl 1.2 g/L Organic matter was removed with H ₂ O ₂ (%30), HNO ₃ (%65-68), and H ₂ SO ₄ (%95-98) Raman microspectroscopy SEM-EDS ICP-MS	963±175.4 items/500 g	PE, PP, PET	Cr: 20.52-42.17 µg/g Ni: 14.63-27.10 µg/g Cu: 11.07-41.55 µg/g Zn: 72.41-199.26 µg/g Pb: 41.93-107.52 µg/g As: 5.84-8.68 µg/g Cd: 0.14-0.89 µg/g Hg: 0.65-1.13 µg/g	Cr: 4.79-15.70 µg/g Ni: 2.11-6.00 µg/g Cu: 2.42-23.25 µg/g Zn: 7.16-185.39 µg/g Pb: 13.42-51.58 µg/g As: 0.64-6.53 µg/g Cd: 0.02-0.78 µg/g Hg: 0.00-0.076 µg/g	[84]
Pearl River Estuary, China	Surface Sediment	Stainless Steel Shovel and Sieve	Washed in aqua regia and H ₂ O ₂ (%30) SEM µ-ATR-FT-IR ICP-MS	328-82276 particles/m ²	EPS	-	Cd: 0.27±0.19 µg/g Cr: 14.9±8.25 µg/g Cu: 15.0±7.66 µg/g Ni: 17.2±17.6 µg/g Pb: 24.8±7.39 µg/g Mn: 730±797 µg/g Fe: 8340±4760 µg/g	[85]

Freshwater Wetlands, India	Sediment	Grab, Mesh sieve	Density separation method with ZnCl ₂ (1.80 g/cm ³) Organic matter was removed with H ₂ O ₂ (%30), HNO ₃ , HClO ₄ and H ₂ SO ₄ Optic Microscope Fluorescence Microscope ATR-FT-IR ICP-MS	2124.84-6886.76 items/kg	PE, PET	As: 17.42-24.74 µg/g Cd: 0.99-6.87 µg/g Cr: 115.78-273.85 µg/g Cu: 75.10-268.53 µg/g Ni: 72.32-87.62 µg/g Pb: 6.09-11.13 µg/g Zn: 204.26-383.22 µg/g	As: 1.56-4.51 µg/g Cd: 0.65-5.78 µg/g Cr: 26.26-342.28 µg/g Cu: 0.29-119.59 µg/g Ni: 12.43-75.77 µg/g Pb: 0.04-104.63 µg/g Zn: 1.88-1191.52 µg/g	[76]
South China Sea, China	Sediment	Stainless steel shovel	Spectrometer ATR-FT-IR LIBS	450 samples	PE, PP, PET, PS	-	Cr: 60.33-75.73 Cu: 10.25-15.32 Fe: 36.66-60.46 Zn: 55.85-80.91 Pb: 30.43-40.56 Cd: 18.33-40.73 Mn: 15.33- 24.78	[86]

(SEM; Scanning Electron Microscopy, EDS; Energy Dispersive X-ray Spectroscopy, FT-IR; Fourier Transform Infrared Spectroscopy, μ -FT-IR; Micro Fourier Transform Infrared Spectroscopy, ATR-FT-IR; Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy, ICP-OES; Inductively Coupled Plasma - Optical Emission Spectrometry, ICP-MS; Inductively Coupled Plasma Mass Spectrometry, AAS; Atomic Absorption Spectroscopy, AFM; Atomic Force Microscopy, LIBS; Laser-Induced Breakdown Spectroscopy, PE; Polyethylene, PVC; Polyvinyl Chloride, PES; Polyether Sulphone, PP; Polypropylene, PS; Polystyrene, PET; Polyethylene Terephthalate, PA; Polyamide, P; Phenolic, EPS; Expandable Polystyrene, As; Arsenic, Al; Aluminum, Cd; Cadmium, Co; Cobalt, Cr; Chromium, Cu; Copper, Fe; Iron, Hg; Mercury, Mn; Manganese, Ni; Nickel, Pb; Lead, Ti; Titanium, Zn; Zinc, HCl; Hydrochloric Acid, HClO₄; Perchloric Acid, HNO₃; Nitric Acid, H₂O₂; Hydrogen Peroxide, H₂SO₄; Sulphuric Acid, NaCl; Sodium Chloride, NaI; Sodium Iodide, ZnCl₂; Zinc Chloride).

TABLE 2. Laboratory simulation tests indicating the adsorption capacities of microplastic particles for some heavy metals.

Experimental media	Treatment methods applied to MPs	Analysis method	Specific surface area	Microplastic concentration	Initial heavy metal concentration	Solution pH	Microplastic polymer type	Adsorption Capacity	References
Milli-Q water	Ball milled (4 h)	FT-IR SEM XPS	0.95 m ² /g	0.02 g	10-50 mg/L	-	PTFE	As (III): 1.03 mg/g	[93]
			0.40 m ² /g					As (III): 0.94 mg/g	
			0.32 m ² /g					As (III): 0.83 mg/g	
Milli-Q water	-	FT-IR SEM EDS	1.4 m ² /g	0.1 g	0.5-32 ppm	6.3	PE	Cr: 4.70 mg/g Cu: 0.259 mg/g Pb: 2.36 mg/g Zn: 0.505 mg/g	[94]
PS							Co: 0.813 mg/g Cr: 0.473 mg/g Cu: 0.358 mg/g Pb: 2.94 mg/g		
PP							Cr: 0.624 mg/g Cu: 2.95 mg/g Pb: 5.55 mg/g		
PVC							Zn: 0.634 mg/g Cr: 2.44 mg/g Pb: 1.90 mg/g		
PET							Pb: 4.93 mg/g		
Seawater			3.2 m ² /g		4-8 ppm	7.72	PE	Cr: 2.56 mg/g Pb: 3.28 mg/g	
PS			Co: 0.4 mg/g Pb: 3.29 mg/g						
PP			Cu: 2.87 mg/g Pb: 3.15 mg/g						
PVC			Cr: 6.14 mg/g Pb: 3.45 mg/g						
			0.59 m ² /g				PVC	Cr: 6.14 mg/g Pb: 3.45 mg/g	
			0.35 m ² /g				PET	Pb: 3.73 mg/g	

Distilled water	-	FT-IR FE-SEM	0.231 m ² /g	40 mg	0-10 mg/L	-	PE	Sr: 470±106 µg/g	[95]
			0.842 m ² /g				PVC	Sr: 790±238 µg/g	
			0.162 m ² /g				PET	Sr: 360±79.2 µg/g	
Distilled water	Washed with HCl and water	FT-IR SEM FAAS EDS	-	1 g	5 mg/L	7.6	High degree PE	Cd: 30.5 µg/g	[96]
High-purity Milli-Q water	-	ATR-FT-IR SEM FAAS	2.11 m ² /g	0.5g	0.05-10 mg/L	-	PE	Cu: 8.46±13.4 µg/g	[89]
<0.001			PS				Cu: 8.28±2.55 µg/g 51.4 µg/g		
0.556 m ² /g			PVC				Cu: 6.29±0.948 µg/g		
0.475 m ² /g			PET				Cu: 8.71±7.74 µg/g; 360±79.2 µg/g		
8.710 m ² /g			PA				Cu: 324±38.2 µg/g and 265±25.7 µg/g		
Milli-Q water	Exposed at UV radiation		0.110 m ² /g				PMMA	Cu: 41.0±1.78 µg/g and 79.4±10.5 µg/g	
Milli-Q water	Ball milled (2 h)	FT-IR SEM XPS	6.77 m ² /g	0.02 g	10-50 mg/L	-	PS	As (III): 0.920 mg/g	[91]
	Ball milled (4 h)		9.25 m ² /g					As (III): 1.047 mg/g	
	Ball milled (8 h)		9.80 m ² /g					As (III): 1.120 mg/g	
-	Natural aged	FT-IR SEM XRD XPS	8.4 m ² /g	0.2-0.6 g/L	2-15 mg/L	5	PE	13.60 mg/g	[97]
-	Washed with HCl and rinsed with water	FT-IR SEM XRD	0.173 m ³ /g	-	-	-	PE	Cd: 36.63 µg/g	[98]
			0.508 m ³ /g				PS	Cd: 40.49 µg/g	
			0.348 m ³ /g				PP	Cd: 36.10 µg/g	
			0.836 m ³ /g				PVC	Cd: 53.48 µg/g	

Distilled water	-	SEM	0.584 m ² /g	45 mg	0-3.4 mg/L	4.5	PS	Sr: 51.4 µg/g	[99]	
			0.314 m ² /g				PP	Sr: 52.4 µg/g		
			0.48 m ² /g				PA	Sr: 31.8 µg/g		
Milli-Q water	Washed with water and oxidized using O ₂ , then stirred at reagent water and air dried	ATR-FT-IR ICP-OES SEM-EDS XPS	0.1036 m ² /g	25 g	1000 mg/L	7.5	LDPE	Cu: 1109 µg/m ² Mn: 199 µg/m ² Pb: 1038 µg/m ² Zn: 893 µg/m ²	[100]	
-	-	FT-IR XPS	-	0.01 g	0.1-2 ppm	4	PS	Cd: 20.154 µg/g	[69]	
Ultrapure water	Fenton aging							Cd: 168.63 µg/g (1 day) Cd: 188.92 µg/g (3 day) Cd: 214.68 µg/g (5 day) Cd: 238.72 µg/g (7 day)		
	H ₂ O ₂ aging							Cd: 44.02 µg/g (1 day) Cd: 54.74 µg/g (3 day) Cd: 67.29 µg/g (5 day) Cd: 76.90 µg/g (7. day)		
Ultrapure water	Rinsed and freeze dried	FT-IR SEM FAAS XRD XPS	-	0.005 - 0.04g	0.1-2 mg/L	-	PS	Pb: 160 µg/g Cu: 210 µg/g Cd: 106 µg/g Ni: 125 µg/g Zn: 78.1 µg/g		[101]

	UV aging in air for 3 months							Pb: 202 µg/g Cu: 173 µg/g Cd: 175 µg/g Ni: 196 µg/g Zn: 183 µg/g	
	UV aging in pure water for 3 months							Pb: 199 µg/g Cu: 176 µg/g Cd: 168 µg/g Ni: 259 µg/g Zn: 312 µg/g	
	UV aging in simulated sea water 3 months							Pb: 199 µg/g Cu: 170 µg/g Cd: 161 µg/g Ni: 211 µg/g Zn: 236 µg/g	
-	Dipped in HNO ₃ , then aged by UV	FT-IR SEM	-	0.5-2.5 g	2-10 mg/L	5	PET	Cu: 375.53 µg/g Zn: 211.03 µg/g	[68]
-	-	XRD FT-IR ICP-AES GC-MS SEM-EDS	0.235 m ² /g	-	0-5 mg/L	5.8	PE	Cu: 27.57 µg/g	[102]
Milli-Q water	Washed and air dried	FT-IR FEI-SEM XPS EDS	4.13±0.4 m ² /g 5.29±0.38 m ² /g 9.51±0.51 m ² /g 1.95±0.29 m ² /g	0.1 g	20-140 mg/L	6	PS PVC PA PET	Cd: 0.76±0.02 mg/g Cd: 1.04±0.03 mg/g Cd: 1.70±0.04 mg/g Cd: 0.25±0.01 mg/g	[103]
Distilled water	-	FT-IR SEM XPS GC-MS	1.3 m ² /g 3.1 m ² /g	10-80 mg	0.1-50 mg/L	6.5	Low degree crystallinity PE High degree crystallinity PE	Cu: 56±2 µg/g Cd: 345±29 µg/g Pb: 590±21 µg/g Cu: 385±39 µg/g Cd: 242±18 µg/g Pb: 2316±283 µg/g	[104]

			2.3 m ² /g				Chlorinated PE	Cu: 3868±98 µg/g Cd: 7485±1544 µg/g Pb: 45306±1109 µg/g	
			8.9 m ² /g				PVC	Cu: 431±11 µg/g Cd: 1748±505 µg/g Pb: 2518±125 µg/g	
Artificial seawater, distilled water	-	FAAS	-	0.05 g	1-10 mg/L	-	Virgin PS	Zn: 0.043-0.204 µg/g Pb: 0.07-0.23 µg/g Cd: 0.031-0.121 µg/g Cu: 0.049-0.227 µg/g	[105]
Milli-Q water	-	µ-FT-IR XPS SEM-EDS	-	0.10 g	0-100 mg/L	-	PE	Pb: 2.01 mg/g	[106]
			-				PP	Pb: 1.57 mg/g	
			794.5 m ² /g				PMMA	Pb: 4.21 mg/g	
Simulated seawater	UV aging for 2 months	µ-FT-IR SEM	-	20 mg	1 mg/L	-	PET	Cu: 0.36 mg/g	[107]
							PA	Cu: 0.30 mg/g	

(SEM; Scanning Electron Microscopy, EDS; Energy Dispersive X-ray Spectroscopy, FT-IR; Fourier Transform Infrared Spectroscopy, µ-FT-IR; Micro Fourier Transform Infrared Spectroscopy, ATR-FT-IR; Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy, FAAS; Flame Atomic Absorption Spectroscopy, ICP-OES; Inductively Coupled Plasma - Optical Emission Spectrometry, ICP-MS; Inductively Coupled Plasma Mass Spectrometry, AAS; Atomic Absorption Spectroscopy, LIBS; Laser-Induced Breakdown Spectroscopy, XPS; X-Ray Photoelectron Spectroscopy, XRD; X-ray Diffraction, GC-MS; Gas Chromatography-Mass Spectrometry, ICP-AES; Inductively coupled plasma atomic emission spectroscopy, FEI-SEM; Field Emission Scanning Electron Microscopy, FE-SEM; Field-Emission Scanning Electron Microscope, LDPE; Low Density Polyethylene, HDPE; High Density Polyethylene, PTFE; Polytetrafluoroethylene, PMMA; Polymethyl Methacrylate, PE; Polyethylene, PS; Polystyrene, PP; Polypropylene, PVC; Polyvinyl Chloride, PET; Polyethylene Terephthalate, PA; Polyamide, PP; Polypropylene, As; Arsenic, Cd; Cadmium, Cr; Chromium, Ni; Nickel, Sr; Strontium, HCl; Hydrochloric Acid, H₂O₂; Hydrogen Peroxide, HNO₃; Nitric Acid).

Polymer Type

Each type of plastic polymers has their own functional groups, specific surface area, polarity and molecular chain organization; leading to differences in affinities for different heavy metal ions [108, 109]. Zou et al. [104] found the affinity of Pb, Cu and Cd for different microplastic polymer types as: CPE > PVC > HDPE > LDPE. They reported that polarity, chemical structure and electronegativity have crucial impact on the adsorption kinetics of HM ions to microplastic surfaces. The high affinity for Cd²⁺ and Cu²⁺ to CPE particles was attributed to the chlorinated polar groups in present in the particles. Yang et al. [89] also stated that polar groups (e.g. -NHCO- and -COO-) are responsible for higher Cu²⁺ adsorption by PA and PMMA. In an experimental study [94], PVC and PE were observed to have a greater affinity for heavy metal ions compared to PET, PP, and PS. PE had the highest adsorptive capability followed by PVC > PS > PP > PET and the researchers attribute this to the rubber-like nature of PE, which probably plays a significant role in its higher capacity to adsorb chemicals.

Specific Surface Area and Particle Size

The specific surface area (SSA) and particle size are considered important parameters for the adsorptive behavior of plastic particles [93]. There are studies showing that smaller microplastics with a larger SSA have a larger adsorptive area for metal ions [74,110]. Although the surface area of microplastics particles with a similar size were found as: PS > PP > PE > PVC > PET, the sorption affinities for metals were found as PE > PVC > PS > PP > PET; probably due to the smaller SSA and pore size [94]. The concentration of lead, copper and cadmium ions adsorbed to PP decreased substantially for larger particles [87]. Cu adsorption to PET and PS were also found to be dependent on particle size; with smaller sized particles (25 µm) having a higher adsorption rate compared to larger ones (180 µm) [111]. They also stated that mass of pollutants adsorbed to MPs were higher for particles with a larger SSA and a smaller particle size.

Crystallinity Structure

Another factor affecting the adsorptive capability of MPs is the crystallinity structure; generally, with a positive correlation between polymer chain organization (i.e. crystallinity) and the adsorptive behavior [88]. For example, the highest cadmium adsorptive potential was recorded for PA which had the highest crystallinity among the polymers with crystallinity with the following order PA > ABS (acrylonitrile butadiene styrene) > PVC > PS > PET; ABS having a lower Cd²⁺ adsorption compared to PVC, PS and PET [103]. Similarly, Zou et al. [104] compared LDPE (which has a lower crystallinity) and HDPE (which has a higher crystallinity) and found that HDPE had a higher affinity for Cd²⁺, Cu²⁺ and Pb²⁺ ions. But they attributed this difference to the chemical structure and electronegativity of particle surfaces, not to the crystallinity of microplastics. Opposite findings are also available showing that high degree of crystallinity can result in a low adsorptive affinity [112].

pH

Researchers revealed that the pH of the experimental media can affect both heavy metal ionization dynamics and the properties of adsorptive surfaces and eventually adsorptive capacity of microplastic particles [68]. Zou et al. [104] recorded that the affinity of copper, lead and cadmium to microplastic surfaces increased as pH increased. Similarly, Li et al. [113] reported that cadmium concentration adsorbed to microplastic particles increased with increasing pH, but then gradually decreased and the highest adsorption occurred in the pH 6-7 range. They attributed this situation to the increases in anionic surface in that pH range [68]. In addition, Wang et al. [114] indicated that the H⁺ ion concentration in the media has a direct effect on the sorption capacity of particles. When the pH is between 3 to 4, there is more H⁺ in the solution which competes with the lead and cadmium ions for surface binding sites on microplastics and as a result decreases the adsorptive behavior of microplastic particles. When the pH is between 4 and 7, adsorption capacity increases since the reactive groups on particles can combine with metal ions easily, and being highest at pH=7. Oppositely, Dong et al. [91] found that the sorption of arsenic ions decreases gradually as the pH increases. Park et al. [115] stated that the competition of the ionic compounds for the active sites on the microplastic surfaces at high ambient pH levels may decrease the adsorption rates.

Temperature

Many studies have shown that solution temperature has a significant and controversial effect on adsorptive potential of microplastic particles for HM ions [93,116]. Heavy metal adsorption to microplastic particle surfaces is an endothermic reaction, thus, increasing temperature may lead to increased adsorption capacity [117]. For example, a rise in the ambient temperature accelerated the sorption of zinc and cadmium ions to plastic particles [68]. There are also contradictory findings; Dong et al. [91] reported that higher temperatures may inhibit adsorption of arsenic ions to PSMPs through the breakdown of H bonds between metal ions and carboxyl groups of particles; thus, leading to a gradual decrease in the amount of As (III) adsorbed. Similarly, Li et al. [118] revealed that binding of Cr (VI) ions to microplastic particles gradually increases as the temperature rises (between 278 K–298 K). They attributed this situation to the accelerated movement of the molecules in the media. However, a negative trend was found showing that if the temperature continues to rise, a marked decrease will be observed in the adsorptive affinity of PE and PS particles. They indicated that increased temperature may lead to activation of desorption between microplastics and heavy metals.

Salinity

Several researchers demonstrated that the salinity of the media may lead to changes in the adsorptive properties of pollutants to microplastic surfaces. For example; Alimi et al. [119] recorded a reduction in the adherence of organic pollutants including PAHs and PCBs to microplastic surfaces with decreasing salinity rates. Barus et al. [105] reported that increasing salinity in the

experimental media decelerates the adsorption rates of HM ions. Additionally, according to Wang et al. [114] salinity can significantly change the capacity of microplastic particles to capture metal ions. They also observed that increasing the sodium chloride concentration in the media led to a reduction in the adhered lead and cadmium ion concentration. The decrease in the concentration of adsorbed Pb ions was attributed to the increased Na⁺ ions in the media which in turn neutralizing the negative charge of particles and inhibiting the adsorption. On the other hand, the decline in the adsorption of copper ions could be as a consequence of the competition of Na and Cu for available surface binding sites on microplastic surfaces which will eventually prevent the electrostatically interactions between copper and microplastic surfaces. Godoy et al. [94] compared the adsorptive properties in aqueous solution and seawater, and found that salinity led to both increases and decreases in the adsorption rates. They stated that, the increase could be due to the conversion of cations on the microplastic surfaces into molecules that can readily adsorb metals. The decreases in adsorption rates were attributed to the competition between cations in adsorptive sites.

Biofilm

Upon introduction to aquatic ecosystems, microplastics (MPs) promptly emerge as favored environments for microbial colonization, due to their advantageous properties. Compared to natural microbial habitats, MPs offer a larger specific surface area, facilitating greater attachment sites for microorganisms. Moreover, their intrinsic hydrophobic nature promotes the development of biofilms, establishing a favorable habitat for microbial growth and activity. The formation of biofilms, which is one of the most important factors that enable heavy metals to adhere to microplastics, has been studied by many researchers. In both in-situ and ex-situ studies, elements such as As, Cd, Au, V, Zn, Pb, Al, Cr, Hg, Mo, and Ni have been reported to accumulate in the biofilm layer of various microplastics (PLA, LDPE, PET, PP, PVC, HDPE, PE, PP) [49, 92, 120-124]. Prunier et al. [125] showed that a large proportion of the Cd, Ti, V, Zn, and Ni heavy metals accumulated on the surface of PE microplastics were adsorbed by the biofilm. In addition, Wang et al. [126] demonstrated that the presence of biofilm on the surface of PS increases the adsorption ratio of Cu and Pb.

Dissolved Organic Matter (DOM)

The adherence of HM ions to microplastic surfaces can be affected by the class and abundance of DOM in the media [127]. DOM can reduce adsorption rates by interacting with the pollutant and thus reduce the available pollutant amount to adhere to plastic particles or by blocking the adsorptive sites on particles [128]. Zhou et al. [103] found that Cd²⁺ adsorption to microplastic surfaces decreased as a result of increased humic acid (HA) concentration in the experimental media. They attributed this decrease to the high affinity of negatively charged HA to cationic pollutants, which leads to competitive adsorption. However, there are also contradictory findings. Guo et al. [98] pointed out that adsorption of cadmium ions to microplastic surfaces increased with increasing HA

concentration, indicating that HA can be adsorbed on certain types of microplastics and therefore, facilitating the ionic bonding with positively charged HMs. Similarly, Wang et al. [114] found that the amount of lead and copper ions adsorbed to new and artificially aged microplastic particles increased with increasing fulvic acid (FA) concentration. They stated that FA was adsorbed to particle surfaces and complexed with metals, thus increasing the adsorptive capability of microplastic particles. Additionally, Li et al. [118] demonstrated that the adsorption of chromium ions on PE and PS particle surfaces was increasing with increasing of FA concentration, whereas for PA, the adsorption of chromium was increased when FA concentration was 1 to 10 mg/L; but continuous rise of the FA concentration led to decrease in the adsorption.

2. CONCLUSIONS

The amount of microplastic particles in the components of the ecosystem including the atmosphere, soil, and the water bodies gradually increased over the last decades. In aquatic ecosystems, microplastic particles can endure for a significant period of time since they are considered as persistent pollutants. Microplastic particles are found nearly in all aquatic habitats, even in alpine lakes and highly isolated water bodies [113]. Microplastic particles can be accumulated in various tissues of exposed animals and can be transported to higher order animals throughout the food chain. Thus, they considered as a major health concern to human beings [129-131]. Additionally, recent studies indicated that microplastics particles create an additional risk by adsorbing heavy metal ions on their surfaces and therefore acting in a similar manner to a Trojan horse [132, 133]. Besides, microplastic particles can accumulate heavy metal ions on their surfaces at a higher rate compared to ambient heavy metal concentrations [62, 75, 76].

The results of both field and laboratory studies reviewed here clearly indicates that several heavy metals including As, Al, Cr, Cu, Pb, Zn, Mn, Co, Cu, Cd and Ni can be absorbed by the plastic particles at high rates depending on several factors. Several factors including the pH and salinity of the media, dissolved organic matter concentration, ambient temperature, specific properties of microplastics (chemical structure, specific surface area, particle dimensions, and polymer chain organization) and ambient heavy metal concentrations have been found to affect the adherence of metals ions to plastic particles [110]. Therefore, it is pivotal to reveal the parameters effective on sorption and desorption dynamics of HM ions to plastic surfaces in order to develop realistic risk assessments. The techniques used in fully controlled experimental designs to simulate environmental degradation-decomposition processes (such as UV exposure, milling, and oxidation treatments) may potentially have an impact on the results obtained; therefore, should be handled carefully. The studies summarized here indicates that more data both from field and laboratory studies is required to comprehend the adsorptive behavior of microplastic particles and to reveal factors effecting sorption of heavy metals to microplastic surfaces.

Author Contribution Statements NSC, ŞK and DN drafted the manuscript and conducted the literature review. MBE conceived of the presented idea and advised on the overall direction and reviewed the manuscript. All authors have read and approved the article.

Declaration of Competing Interests The authors declare no conflict of interest.

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