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Review

A Scienciometric Review On Microplastics As Chemical Pollutant Vectors In Aquatic Ecosystems

Mariangela Rodrigues Gonçalves[1], Júlia Vianna de Pinho[2],[3], Rachel Ann Hauser-Davis[4*]

[1] Universidade Federal do Rio de Janeiro, Av. Carlos Chagas Filho, 373, Rio de Janeiro, RJ, 21941-590, Brazil.

[2] Programa de Pós-Graduação em Vigilância Sanitária (PPGVS), Instituto Nacional de Controle de Qualidade em Saúde (INCQS), Fundação Oswaldo Cruz (FIOCRUZ), Rio de Janeiro, RJ, 21040-900, Brazil.

[3] Núcleo de Análise de Alimentos (NAL), Laboratório de Apoio ao Desenvolvimento Tecnológico (LADETEC), Universidade Federal do Rio de JAneiro (UFRJ), Cidade Universitária, Rio de Janeiro, RJ, 21941-598, Brazil

[4] Laboratório de Avaliação e Promoção da Saúde Ambiental (LAPSA), Instituto Oswaldo Cruz, Fundação Oswaldo Cruz, Av. Brasil, 4.365, Manguinhos, Rio de Janeiro, RJ, 21040-360, Brazil.

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Abstract

The production and disposal of plastic material has increased exponentially in recent decades. As a result, microplastics resulting from plastic degradation processes are now present in all environmental compartments, in particular, aquatic ecosystems. These microparticles can interact with different chemical pollutants, representing a significant risk to living organisms. In this context, the present study aimed to assess microplastics as chemical pollutant vectors in aquatic ecosystems, evaluating adsorption processes between these particles and both organic and inorganic pollutants. To this end, a scienciometric review was carried out, retrieving a total of 56 scientific articles. The retrieved studies indicate microplastic particles are capable of associating with different environmental chemical contaminants and that interactions depends on abiotic factors such as pH, salinity, light and temperature, the type of polymeric material and its aging characteristics and, finally, the organic matter adhered to the particle. Further studies on this topic are required to understand potential deleterious effects on aquatic biota due to microplastic-adsorbed chemical pollutants and establish measures capable of reducing and controlling these pollutants.

Keywords: Polymers; contaminant transport; adsorption; anthropogenic impacts.

*Corresponding author: rachel.hauser.davis@gmail.com

INTRODUCTION

Plastics are highly resistant synthetic materials derived mainly from oil and natural gas, consisting of polymers, which in turn are materials formed by macromolecules, composed of several smaller units, called monomers. These polymers can be of natural origin, such as rubber and shellac, for example, or synthetic, such as polycarbonate and polyethylene (Gorni, 2003). These materials became popular at the end of the 20th century thanks to their low production cost, durability and malleability, focused on single-use utensils, such as food packaging, bags and bottles, with over 15 different types of polymers synthesized (Andrady & Neal, 2009).

Every year around 400 million tons of plastic are manufactured worldwide, mostly polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-intensity polyethylene (LDPE) and polypropylene (PS) (Olivatto *et al.*, 2018), with less than 10% of this total being recycled. From 1950 to 2017, about 9.2 billion tons of plastic were produced (Zamora *et al.,* 2020). In 2019, more than 130 million tons were incinerated, disposed of in landfills or directly into the environment, much of it ending up in the oceans, the final sink of most environmental contaminants (Charles *et al.*, 2021). Carried by currents, this plastic waste accumulates in large concentrations in ocean gyres in the north and south of the Atlantic, north and south of the Pacific and in the Indian Ocean, commonly called garbage patches (Figure 1) (Elías, 2015).

According to the World Bank report, Brazil is the fourth country to produce plastic waste in the world, generating slightly over 11 tons per year (Figure 1), behind India with about 19 tons, China with approximately 54 tons. and the United States with almost 71 tons. This value refers to all plastic waste discarded, from different sources, in a one-year period (Kaza *et al.*, 2018).

Figure 1. Rank of countries that produce the most plastic waste, in tons per year and the location of ocean gyres. Source: Adapted from Zamora *et al.* (2020).

These huge amounts of plastic waste becomes a significant danger to aquatic ecosystems, as they can undergo decomposition due to abiotic factors, such as light and temperature, fragmenting into smaller particles, known as microplastics. These materials display enormous toxic potential to living beings and can be transferred through the trophic chain, causing risks to both animal health and human health (Thompson *et al*., 2004).

Microplastic particles were initially described in 1972 by Carpenter and Smith, but this term only became widely employed after the study carried out by Thompson *et al.* (2004). Many size variations have been employed to define microplastics over the years. In 2008, at the workshop held by the National Oceanic and Atmospheric Administration (NOAA), which aimed to discuss the problems and possible paths for future research related to microplastics, it was defined that these are plastic particles smaller than 5 mm, and, according to Rafiee *et al.* (2018), when smaller than 1 µm, are considered nanoplastics. In addition, microplastics are also classified as primary and secondary. Primary ones are those produced in micro size, for the manufacture of other products and the secondary ones are those from the fragmentation of larger plastics due to physical-chemical environmental factors (Arthur *et al.*, 2009). It is estimated that 5 trillion particles from both primary and secondary sources pollute the ocean surface (Alimi *et al.,* 2018).

In recent years, some studies have analyzed microplastic bioaccumulation in marine animals such as fish, turtles and sea cucumbers (Boerger *et al.*, 2010; Graham & Thompson, 2009; Lazar & Gračan, 2011). When reaching nano size (<1 µm), these particles can be absorbed by organisms and cross immunological barriers, affecting organs, tissues and even cell functionality, also causing toxic or lethal (Rafiee *et al.*, 2018).

Studies have also investigated microplastic potential as vectors for different chemical pollutants, such as metals

and persistent organic pollutants (POPs) (Hartmann *et al.,* 2017; Rios *et al.*, 2007), assessing factors that contribute to adsorption dynamics, such as type of polymer, aging of the material and aggregated organic matter (Carbery *et al*., 2020; Fang *et al.,* 2019; Mendoza & Jones, 2015). The greatest concern regarding chemical pollutant adsorption onto microplastics is a significant bioaccumulation potential and their harmful potential for biota and humans (Turner & Holmes, 2015).

In this context, this study aims to discuss the potential of microplastics as chemical pollutant vectors in aquatic ecosystems.

METHODOLOGY

A descriptive research following a scientometric review comprising a quali-quantitative approach was adopted.

All searches were carried out from June 2021 to September 2021, through online consultation at the Web of Science, Google Scholar, Scielo and PubMed databases, comprising papers from 2005 to 2021, written in Portuguese or English, employing the following keywords: Microplastics PAH adsorb/Microplastics adsorption HPA; Microplastics metal adsorb/Microplastics metal adsorption; Microplastics pharmaceuticals adsorb/Microplastics pharmaceuticals adsorption; Microplastic POP adsorb/Microplastic POP adsorption; Microplastic PFAs adsorb/Microplastic adsorption PFAs; Microplastic Vector/Microplastic Vector.

RESULTS AND DISCUSSION

A total of 56 articles were retrieved, categorized as displayed in Figure 2 into field, field-laboratory and laboratory studies per country of publication. China represented the most field studies (n = 5), followed by India (n = 2) and Indonesia (n=2). Of the ten countries regarding field studies, six were conducted on the Asian continent and three were from different continents (American, Australian and European), demonstrating the interest of Asian countries in this topic. Of the seven countries regarding field studies, three were Asian and four European, but in quantitative terms, the Asian continent produced more studies than the others, totaling 10 articles. The studies conducted in the field and laboratory consisted of investigations in which microplastic materials were extracted from natural environments for subsequent adsorption testing with specific types of selected chemical contaminants in the laboratory, or alternatively, new (virgin) microplastics were used, which were then exposed to natural conditions in the field, to create conditions similar to those of plastic materials already present in these aquatic environments, for a comparative analysis of adsorption between such aged materials and virgin particles analyzed in the laboratory. Similar scientific production was noted between continents addressing the topic, as, of the six analyzed countries, two were Asian, three European and one American. Concerning the total number of studies, four papers were published in Europe, two in Asia and two in America.

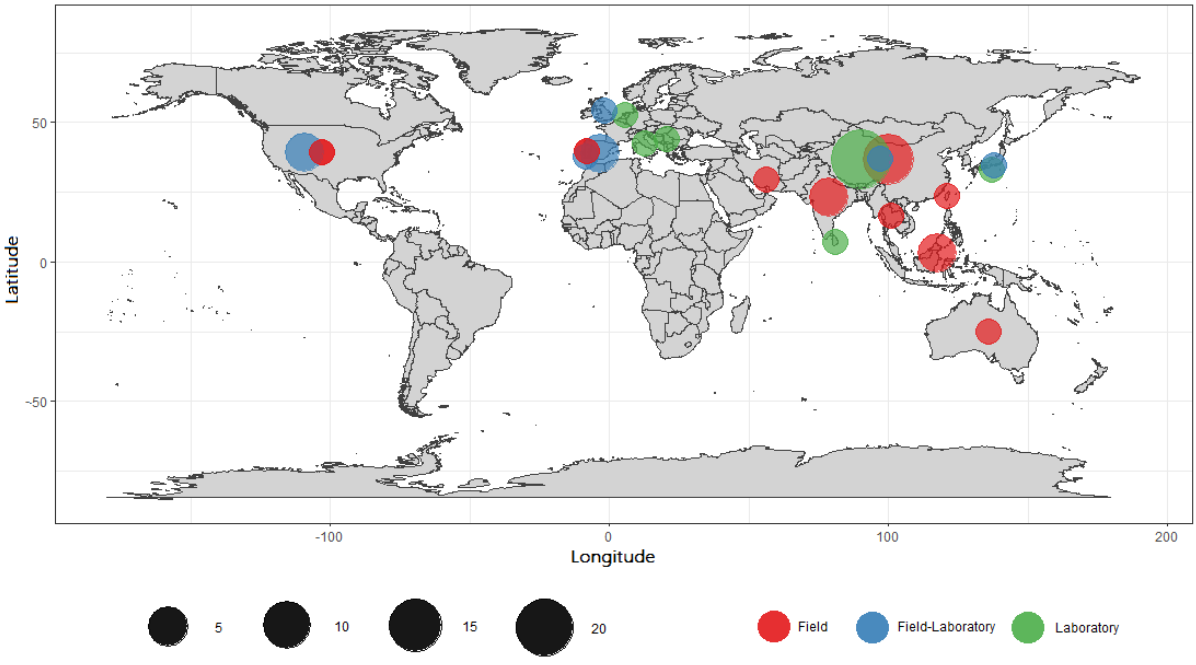

Figure 2. Map categorizing retrieved studies as field, field-laboratory or laboratory only studies per country.

Chemical contaminant and habitats analyzed in the retrieved studies are displayed in Figure 3A and 3B, respectively. Regarding the different chemical contaminants assessed by the retrieved studies, field studies were distributed mostly between research on metals and polycyclic aromatic hydrocarbons, with PAH, PCB, PFAS and DDT assessments in one paper each. Concerning laboratory studies, pharmaceuticals were the most investigated, followed by BPA, metals, DBP, PAH, pesticides and POPs in general. The same trend for a higher number of studies concerning metals was also noted for field-laboratory studies, followed by PFAS and pharmaceuticals. Regarding the habitats analyzed in the retrieved surveys, field and field-laboratory studies explored different aquatic ecosystems. Several types of ecosystems were assessed, but well-distributed among saltwater and freshwater environments. Most assessments considered seas, rivers and bays/estuaries.

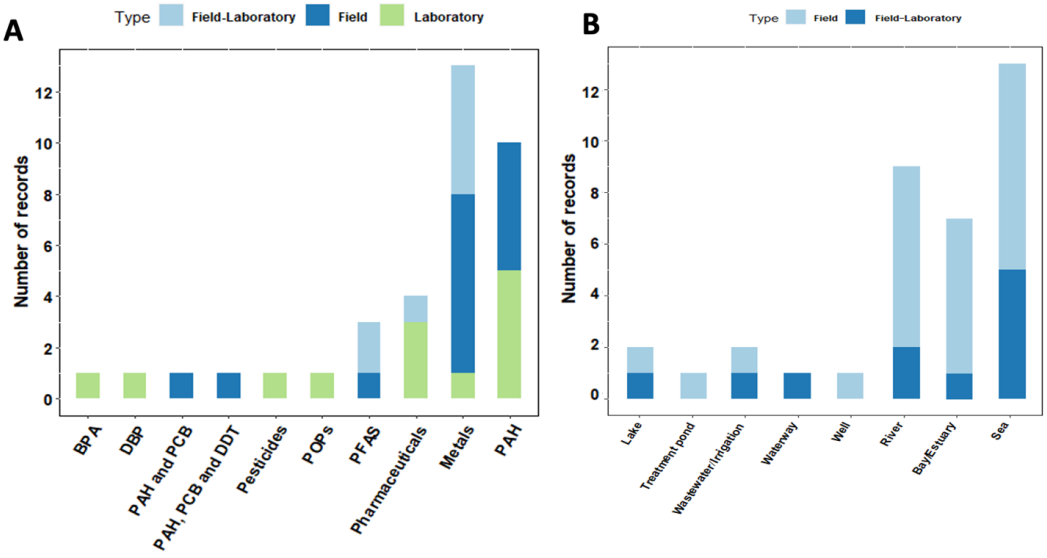

Figure 3. (A) Distribution of analyzed pollutant classes among field, laboratory and field-laboratory studies retrieved in this scientometric review; (B) Aquatic habitats analyzed in field and field/laboratory research.

The impact factors of the journals that published field assessments are displayed in Figure 4. Journal impact factors varied greatly, only one below 3.00 and the rest ranging from 3 to 11, indicating high interest in microplastics assessments.

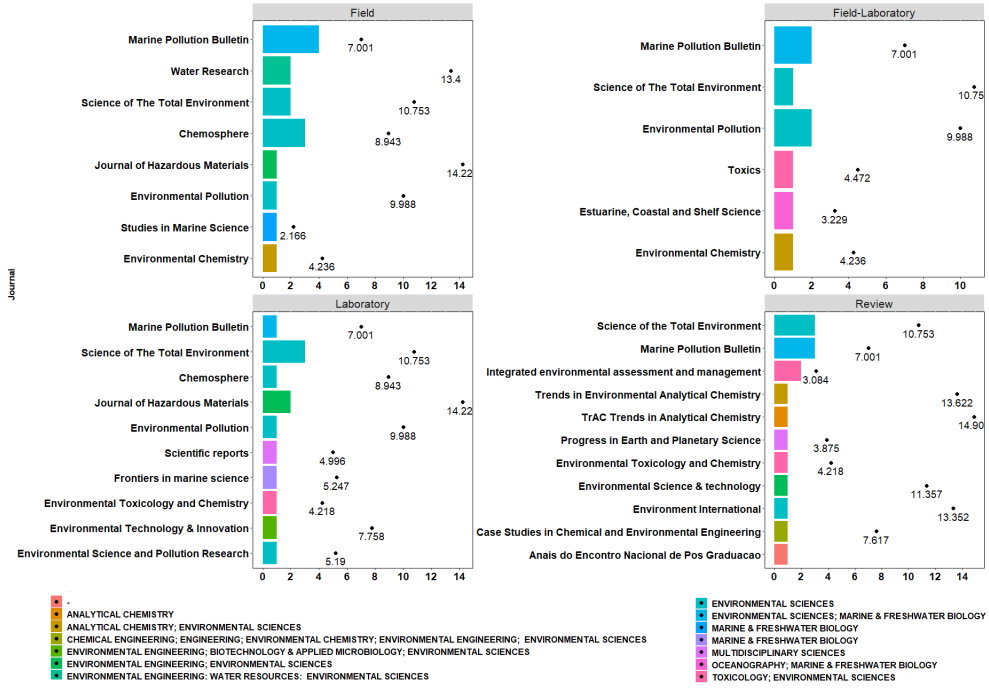

Figure 4. Journal impact factors of the published papers retrieved in this scientometric review. Impact factors are up to date (CAPES, 2022).

DISCUSSION

To understand the adsorption dynamics that involve synthetic polymers and chemical pollutants, factors that contribute to this mechanism should be discussed. Depending on environmental conditions and polymer properties, pollutants can either adsorb or desorb from microplastic particles, similarly to sediments and fine particulate matter (Mendoza & Jones, 2015; Rocha *et al.*, 2009). Adsorption is a physicochemical event that occurs when substances in liquid or gaseous form adhere to the surface of solid particles. The elements transferred to the surface are called adsorbate, whereas the solid particle that retains the material is called adsorbent. When the separation of these components occurs, it is called desorption (Andia, 2009). Adsorption and desorption processes are closely linked to physicochemical characteristics of the investigated substances, the solid material and the environment in which they are in. Specific surface areas, electrostatic interactions, changes in pH, light levels and temperature are direct drivers in this regard. To understand and estimate the transition from pollutants to solid particles, some parameters are routinely employed, such as the partition or distribution coefficient, which indicates the ratio of the pollutant concentration between the liquid medium and the concentration in the solid, considering equilibrium conditions. Additionally, the octanol-water partition coefficient may be determined to estimate the behavior of hydrophobic compounds that do not interact with the surface of solid particles. (Freitas *et al.,* 2022). Figure 5 presents some factors that enable the adsorption dynamics between microplastics and different chemical pollutants.

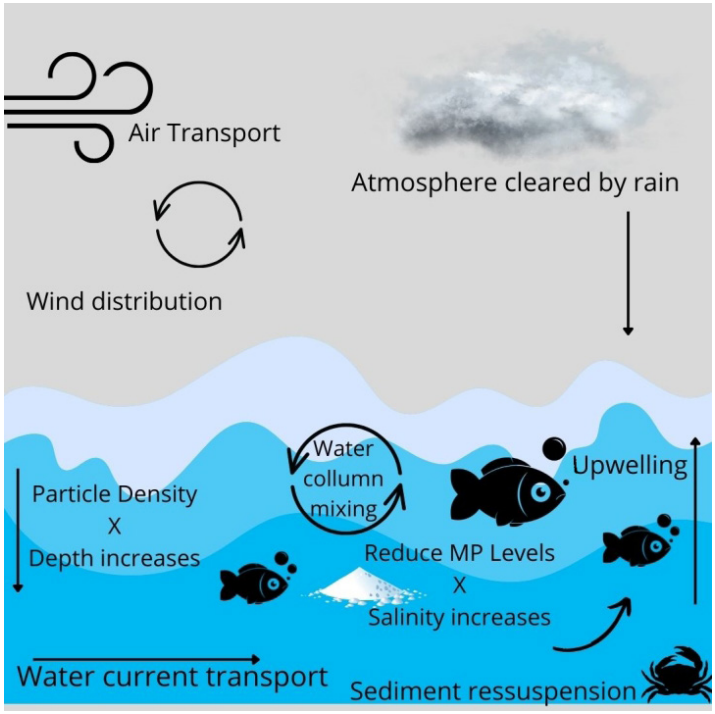

Figure 5. Environmental factors that influence the adsorption dynamics between chemical pollutants and microplastics. Adapted from Atugoda *et al.* (2021).

Given the data reported herein, it is imperative to discuss the relationship between microplastics and different chemical pollutants. In order to comprehensively understand the adsorption dynamics of microplastics and the aforementioned substances, it is imperative to identify factors that contribute to this mechanism. Therefore, the following discussions will be presented based on chemical pollutants classess. Additionally, insights from relevant literature reviews consulted for this study are also discussed.

Each chemical pollutant class assessed in the retrieved studies shall be discussed separately.

Metals

In relation to the evaluated metals, despite different adsorptions, depending on the material, environment and type of metal, many analyzed characteristics showed similarities. The following studies evaluated the processes related to adsorption dynamics between sediments and virgin and aged plastic particles to understand factors that influence metal adsorption processes.

Gao *et al.* (2019) carried out a field study along three sites on the coast of China and compared the results to laboratory analyses, assessing different-sized polypropylene particles (2 mm, 3 mm, 4 mm and 5 mm) and their relationship with lead, copper and cadmium. The authors report that adsorption

was lower with increasing particle sizes, associated with higher surface area-volume ratios. They also observed a higher affinity for aged microplastics compared to virgin pellets and evaluated the adsorption capacity of metals on different microplastic types, namely polyvinyl (PVC), polypropylene (PP), polyethylene (PE), polyamide (PA), and polyformaldehyde (POM). Lead, copper and cadmium adsorptions were higher to PVC and PP particles. Finally, the authors also compared metal and polycyclic aromatic hydrocarbons (PAH) adsorptions and reported similar adsorption to PP particles.

In this regard, Carbery *et al*. (2020), collected microplastic samples at 37 sites along the Australian coast, reported the presence of arsenic, barium, lead, chromium, copper, selenium, manganese and zinc, with higher concentrations in aged microplastics compared to the study conducted by Gao *et al.* (2019), who determined several metals adsorbed to virgin microplastic samples). The study took place in industrial, urban and rural areas, and the highest metal accumulations were observed in samples from industrial areas, as expected. Thus, the authors indicate that plastic particles can adsorb differential metal concentrations depending on their location.

In another study, Brennecke *et al.* (2016) carried out a field study at the Marine Biology Station of Funchal, located on the south coast of Madeira Island, in Portugal, reporting after 14 days of experiment, aged microplastics did not reach equilibrium, whereas virgin particles reached constant concentrations copper. This study evaluated the adsorption of copper and zinc extracted from an antifouling paint in sea water and compared it with virgin polystyrene (PS) and aged polyvinyl (PVC) microplastic. Both materials were able to adsorb metals, but the aged material adsorbed higher concentrations of pollutants due to its irregular surface and adhered organic matter.

Guan *et al.* (2020) compared microplastic particles with biofilm and natural sediments in an urban lake and reservoir located in China and reported that the presence of biofilms increased metal adsorption capacity, as it is able to alter physico-chemical surface properties. Thus, the interaction between metals adsorbed to virgin microplastic was lower than in microplastics with biofilm, but natural substrates displayed greater adsorption capacity.

In a similar assessment, Besson *et al*. (2020) collected sediment samples in Japan for later comparison with virgin polyethylene under laboratory conditions. The sediments were treated with successive washings in osmotic water, sieved, sterilized and stored at 4°C. The authors report that cadmium, cesium and zinc adsorptions were higher in sediment particles than in virgin microplastics and even weathered microplastics with biofilm formation, although this study highlights that with the constant increase of these contaminant particles in the aquatic environment, this issue is paramount in these types of studies.

Gao *et al.* (2019) carried out a field study along three sites on the coast of China and compared the results to laboratory analyses, assessing polypropylene particles of different sizes (2 mm, 3 mm, 4 mm and 5 mm) and their relationship with lead, copper and cadmium. The authors report that the adsorption is lower with increasing particle sizes, associated with the surface area-volume ratio. They also observed a higher affinity for aged microplastics compared to virgin pellets and evaluated the adsorption capacity of metals on different microplastic types,namely polyvinyl (PVC), polypropylene (PP), polyethylene (PE), polyamide (PA), and polyformaldehyde (POM). Adsorption of lead, copper and cadmium was higher in PVC and PP. Finally, the authors also compared metal and polycyclic aromatic hydrocarbons (PAH) adsorptions and reported similar adsorptions PP particles.

According to Selvam *et al.* (2021), who analyzed microplastic samples in groundwater and surface waters off the southern coast of India, PP can more easily adsorb arsenic, cadmium, chromium, copper, lead, manganese and zinc, whereas PA only adsorbs manganese. Furthermore, both types of microplastics can adsorb arsenic, cadmium and zinc, even at low concentrations, from the aquatic environment.

Those findings corroborate Ta and Babel (2020), who identified that most of the microplastic found in the Chao Phraya River, Thailand, was PP, both in water and in sediments, and the highest adsorbed metal concentrations were lead and copper compared to nickel and chromium, which were also identified.

Purwiyanto *et al.* (2020) also analyzed the occurrence of lead and copper along 10 stations of the Musi River, in Indonesia, reporting higher values of these metals adsorbed on microplastics than in the river water itself. The authors also indicate that lead concentrations were higher than copper in the plastic particles and that lead accumulation in the water increased when reaching the estuary, while copper content remained stable along the way. It is interesting to note that metal concentrations increased in the estuarine region of the river. Thus, it is clear that chemical factors, such as water pH and salinity can increase or decrease metal adsorption.

Godoy *et al.* (2019) in a field and laboratory study, acquired samples of different polymers and compared adsorption dynamics in different water samples, namely, ultra purified water, water collected from the Mediterranean Sea off the coast of Granada (Spain), water collected from an urban wastewater treatment plant in Granada (Spain) and irrigation water from the fertile plain of Granada (Spain). They found that the organic matter present on the microplastic increased lead and chromium adsorption, but that water pH altered these dynamics. For example, sea water both increased and decreased metal adsorption. Copper and chromium adsorbed well on PP and PVC, while chromium and cobalt decreased on PE and polystyrene particles. In this sense, it was difficult to establish an adsorption pattern, as alterations may be due to salinity and/or other chemical aspects, or still, a combination of several factors.

Turner and Holmes (2015) compared virgin and aged pellets employing water samples from a river and from the

sea, and aged microplastics from a beach, all located in England, also assessing virgin pellets from a factory in the United Kingdom and later analyzed adsorption with added metals under laboratory conditions. The authors report higher cadmium, cobalt, nickel and lead adsorption in the river and chromium was higher in the seawater, attributing this to the fact that the pH of the river (6.5) is lower than that of the sea (8.0), as well as other physico-chemical factors.

Some authors have pointed out the toxicological risks that these elements represent for marine animals. In this regard, Sarkar *et al.* (2021) in a study carried out in India reported microplastics collected from wastewater channels and treatment ponds adsorbed different elements (arsenic, cadmium, chromium, copper, nickel, lead and zinc) according to the type of metal and habitat, further demonstrating that swamps have been contaminated with microplastics due to wastewater sources containing high amounts of toxic metals, contaminating fish both by the ingestion of contaminated food items and metal-contaminated microplastics..

Another laboratory study performed by Wang *et al.* (2020) exposed cadmium to aged polyethylene microplastic for 7 days and evaluated the effects of adsorbed particles and particles without the metal in *Moina monogolica* cladocera over a period of 21 days. The experiments revealed that the microplastics containing the adsorbed metal caused greater adverse effects to exposed organisms than the non-adsorbed microplastic. Furthermore, the cadmium-containing particles, in addition to causing internal injuries when ingested, can affect reproduction and cause poor nutrition in offspring, which can lead to death and consequently, negative ecosystem effects. Finally, Foshtomi *et al.* (2019) reported a strong relationship between microplastic abundance, metals (aluminium, arsenic, cadmium, cobalt, chromium, copper, iron, mercury, manganese, nickel, lead, titanium and zinc), polycyclic aromatic hydrocarbons and total petroleum hydrocarbons in surface sediments collected in Iran. Among the detected PAH (naphthalene, acenaphthene, fluorene, phenanthrene, pyrene, benzo (a) anthracene and benzo (a) pyrene), naphthalene and benzo (a) anthracene were the most abundant. The authors suggest that these toxic pollutants can be ingested by benthic animals, contributing to biomagnification along the food chain, as these animals live in close contact with sediments.

Persistent Organic Pollutants (POPs)

Regarding POPs, studies were retrieved on, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dibutylphthalate, pesticides and per and polyfluoroalkylated substances, and reported adsorption dynamics were very similar to metal microplastic adsorption.

As in previous studies, the size of the plastic particles was an important factor regarding adsorption. In a field study in the North Pacific Gyre, Mendoza and Jones (2015) observed that smaller particles agglutinated more toxic material compared to particles larger than 0.5 mm in seawater samples. The samples contained PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (b) fluoranthene, benzo (a) pyrene, benzo (h,g,i) perylene, dibenzo (a,h) anthracene and indenol (1,2,3,-cd) fluoranthene) and polychlorinated biphenyls. Concentrations varied greatly due to location and type of plastic. In addition, the authors pointed to the fact that the plastic particles presented a similar adsorption dynamic to sediment particles, although they remain floating on the surface of water bodies, becoming available to the local biota and increasing contaminant desorption and bioaccumulation risks.

One laboratory study also evaluated particle size influence on chemical contaminant adsorption dynamics (Liu *et al.,* 2016), where the authors analyzed the sorption of polycyclic aromatic hydrocarbons (phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene and benzo (g, h,i) perylene) onto plastic nanoparticles up to 70 nm, in fresh water and observed that the nanoplastic particles exhibit a stronger sorption than microplastic particles. This is of significant concern, as microparticles suffer with the action of time and degrade until reaching nano sizes. Other studies have pointed to the ability of nanoparticles to cross the blood-brain barrier (Koziara *et al.*, 2003) and penetrate the chorion of fish eggs (Oryzias lapides), gills and intestines in adulthood (Kashiwada, 2006), demonstrating significantly high risk to aquatic biota.

These is similar to the study conducted by Chen *et al.* (2020), who collected surface water samples from an estuary at port entrances in Taiwan, reporting microplastics carrying PAH (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(k) fluoranthene, benzo(b)) fluoranthene, benzo (a) pyrene, benzo (h,g,i) perylene, dibenzo (a,h) anthracene and indenol (1,2,3,-cd) fluoranthene) in about 10% of the total zooplankton in the area, with the contaminants mostly petrogenic in origin. The vast majority of these particles ranged between 0.33 and 2 mm, and the most abundant types were PE and PP, with other types representing less than 5%.

In addition to size, other studies have verified the role of light and temperature in interactions processes between microplastics and chemical contaminants. For example, Ye *et al.* (2020) analyzed the desorption of dibutyl phthalate (DBP) from polyvinyl microplastics, carrying out experiments with PVC tube fragments placed in glass flasks containing pure water, under equal natural light and temperature conditions, with changes applied throughout the process to better understand chemical-microplastics dynamics, followed by the introduction of a low-density polyethylene material fixed to a copper wire to adsorb the particles released from the PVC. The authors observed the influence of light on DBP leaching, which accelerates the aging process of microplastics and contributes to contaminant degradation, increasing release rates. Particle

size was also shown to influence the release of DBP, with smaller particles exhibiting greater surface area in contact with the water, facilitating desorption. At the same time, the degradation of these plastic particles into smaller pieces damages the material structure, contributing to contaminant releases. Finally, temperature was the most significant factor, increasing DBP release with increasing temperatures. The authors, therefore, point out that microplastics, when ingested by aquatic organisms, may release high contaminant loads due to higher body temperature.

In line with this, Noro and Yabuki (2021), in a laboratory study, confirmed the photolysis of PAH (fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(j)fluoranthene, benzo(e) pyrene, benzo(b)) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene and benzo (g,h,i) perylene) adsorbed on microplastics by means of sunlight, tested in both pure water and in a nitrate solution. The authors also indicated that photolysis is directly linked to water depth, since sunlight only reaches up to a certain depth. Thus, field studies carried out on surface waters may underestimate real microplastics concentration and, consequently, the potential risk of these pollutants. In addition, the nitrate experiment increased the photolysis of PAH adsorbed on microplastics, which may indicate high concentration rates of adhered PAH in coastal areas than in the open sea, due to higher nitrate rates and their consequent influence on photolysis as a degradation pathway.

Another aspect addressed in the retrieved studies was sample location since, the environmental profile of the study area and greater or lesser anthropic influence can also contribute to high pollutant levels and altered physical-chemical environmental factors. In this regard, laboratory assessments tend to assess toxic effects and behavior, while field assessments display the reality of contamination status.

In this regard, Bouhroum *et al.* (2019) sampled microplastics in the North Atlantic Gyre and coastal areas of Indonesia in a field study to evaluate different concentrations of polycyclic aromatic hydrocarbons and adsorbed PCBs, noting that coastal samples exhibited high concentrations of low molecular weight PAH and highly chlorinated PCBs, whereas samples from the North Atlantic gyre contained lower contaminant concentrations, although comprising high molecular weight PAH and low-chlorinated PCBs. The authors indicate this as due to the degradation of these pollutants along ocean currents or in the atmosphere.

In order to assess anthropic impacts and associations to microplastics as chemical pollutant vectors, Cheng *et al.* (2021) collected microplastics from eight rivers that drain into the Pearl River estuary, in China, and analyzed perfluoroalkylated substances (PFAS) concentrations. The authors indicate that microplastics sampled from drainage areas close to urbanization areas exhibited higher adsorbed PFAS values than drainage areas close to agricultural and forestry areas, which, interestingly, varied according to the season of the year, higher during the dry season and lower in the rainy season.

In another study, Tang *et al.* (2018) studied the amount of microplastics and associations with polycyclic aromatic hydrocarbons, comprising 3- and 4-ringed PAH and alkylated PAH in coastal areas of Xiamen, China, to assess the influence of human activities, given the significant increases in industrialization processes and urbanization in that area. The authors reported that the plastic particles were significantly associated to PAH and that most of the plastic material detected at the study area comprised polyethylene and polypropylene. The authors also indicate the influence of increasing urbanization rates and river flows.

Camacho *et al*. (2019), in a study carried out in the Canary Islands, analyzed the adsorption of organic pollutants to microplastics, investigating both pellets and weathered plastic fragments. They identified the presence of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), bromoodiphenyl ethers (BDEs), as well as organophosphate flame retardants (OPFRs), sunscreens (UV filter) and the pesticide chlorpyrifos. The data indicated that tourist regions exhibited very high levels of adsorbed chemical pollutants compared to desert regions, indicating significsnt anthropogenic contaminant contributions levels. The authors also reported that contaminant levels adsorbed on plastics were high, similar to industrialized areas, and that the presence of UV filters on microplastics was higher in beaches very frequented by bathers, indicating that part of the detected pollution occurs in specific locations.

Furthermore, the type of material also interferes in the adsorption mechanism of pollutants, as demonstrated by Frias *et al.* (2010), who collected microplastics on two Portuguese beaches (Cresmina and Fonte da Telha) and detected 16 priority PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, perylene, indene(1,2,3-cd)pyrene, and benzo(g,h,i)perylene), PCBs and Dichloro-Diphenyl-Trichloroethane (DDTs), mainly adsorbed onto black pellets. The PAH concentrations detected on microplastics from Cresmina beach, were higher in black pellets and on Fonte da Telha beach, in aged pellets. Likewise, PCBs levels were also high on black pellets, but low on white pellets. According to the authors, this may be associated to the type of material used in different-colored pellets, as black ones were mostly made of polypropylene and polystyrene, while the aged ones were made of polypropylene and polyethylene.

In a study carried out in a laboratory in Serbia, Lončarski *et al.* (2021) demonstrated that physicochemical plastic factors, such as granulation, porosity, surface area and structure, directly influence pollutant adsorption. The authors reported that the highest pollutant rates were detected in microplastics extracted from cosmetic products and the lowest were detected on granules, with the highest adsorption levels noted for polypropylene and the lowest, for polylactic acid (PLA). The authors also highlighted the importance of new studies to evaluate the real environmental condition in relation to

particles present in cosmetic products, also highlighting that PLA particles display a lower effect on PAH transport, due to lower adsorption rates.

The presence of biofilms and organic and inorganic material on microplastics also favor adsorption, produced by Proteobacteria (92.34%) in the Shitoukoumen Reservoir, and by Proteobacteria (58.37%) and Cyanobacteria (35.43%) in the Nanhu Lake (Guan *et al.*, 2020). In this regard, Scott *et al.* (2021) conducted both field and laboratory studies to observe the interaction between PFASs and microplastics, quantifying PFAS in different polymer particles left in a lake for 3 months and then analyzed in a controlled environment for 1 month to assess adsorption without the presence of organic and inorganic matters adhered to the materials. The verified greater adsorption rates in microplastics inserted in the lake than those without organic and inorganic material used in the laboratory, pointing to the importance of this component in increasing PFAS microplastic adsorption. The authors also pointed to variations in adsorption rates in the different particles present in the lake (24- to 259-fold higher than water concentrations), suggesting that this takes place due to the different amount of organic matter and biofilms present on different types of particles.

Different physico-chemical aspects, such as hydrogenic potential (pH), plastic aging, hydrophobicity, hydrogen bonds and the electrical properties of the particles, are the main chemical pollutant absorption drivers.

To understand some of these processes Llorca *et al.* (2018) analyzed three different types of microplastics, polyethylene (PE), polystyrene (PS) and polystyrene carboxylate (PS-COOH), and their sorption relationship with 18 types of perfluoroalkylated substances (in addition to carboxylic acids, sulfonates and a sulfonamide) in aquatic ecosystems, acquiring microplastic samples from two companies in the United States and collecting water samples from a river and beach in Spain. The authors observed that microplastic particles can adsorb PFAs from surface waters, with adsorption greater in aged and/or smaller particles. Furthermore, pH can alter electrostatic interactions, changing the surface charge of microplastics. The analyses also indicated that perfluorosulfonates and sulfonamides display a higher propensity to adsorb to microparticles, while PFAs adsorb at higher rates to polystyrenes compared to polyethylenes.

In this regard, Li *et al.* (2020) carried out a laboratory study in China, aiming to create a computational method capable of more quickly observing organic pollutant adsorption to microplastics, in aquatic environments under different pH conditions. To this end, five quantitative structure-property relationship (QSPR) models were performed to measure this capacity in polypropylene and polystyrene particles in seawater only and polyethylene in seawater, fresh water and pure water. Hydrophobic interactions proved to be an important factor for adsorption in all evaluated models, and hydrogen bond interactions and covalent acidity interactions were proven relevant for all polymers in seawater.

In a study carried out in a crab and fish farm in China, Wang *et al.* (2018) analyzed the sorption of phenanthrene (hydrophobic) and phenol (hydrophilic), identifying various plastic particles, including polyethylene and nylon. Polyethylene exhibited a higher phenanthrene adsorption capacity than nylon, due to its small size and weathered surface, which facilitate sorption processes. In another assessment, Wu *et al.* (2019) investigated five bisphenol analogs (BPA, BPS, BPF, BPB and BPAF) in order to understand adsorption on polyvinyl (PVC) microplastics. Adsorption was noted due to hydrophobic interactions, while electrostatic forces inhibited the process. Hydrogen and halogen bonds also aided in adsorption to PVC.

Apart from hydrophobic factors, electrical properties are also important concerning microplastic contaminant loads. In this regard, Yu *et al.* (2020) analyzed polystyrene microplastics with no carboxyl group modifications in the laboratory, as microplastic aging contributes to the emergence of carboxyl surface group (Lin *et al.*, 2020), to assess potential alterations in the adsorption dynamics of naphthalene and its derivatives. The authors observed that unloaded naphthalenes and derivatives displayed higher sorption capacity in relation to loaded naphthalene derivatives regardless of non-microplastic carboxyl groups, due to the hydrophobicity of naphthalene and its derivatives and the electrical properties of the surface of the polystyrene particles. The authors pointed out that, despite the sorption capacity of these derivatives, they may be the same or less than naphthalenes, and it is important to note that the degree of toxicity of these derivatives is probably higher.

An important point made by Wang *et al.* (2020), was in relation to the degradation half-lives of pesticides in a laboratory study carried out to observe polyethylene microplastics and their adsorption and desorption dynamics with pesticide residues (epoxiconazole, tebuconazole, mycobutanil, azoxystrobin, simazine, terbuthylazine, atrazine and metolachlor) in the aquatic environment. The authors observed that the presence of polyethylene microparticles reduced pesticide residues when in water and adsorption reached a maximum limit on the first day of the experiment, decreasing thereafter due to contaminant degradation. Although that study did not observe adsorption changes in relation to aged plastic particles, microplastics considerably increased the degradation half-lives of the assessed pesticides and, therefore, increased their persistence in the aquatic environment.

Significant toxicological risks concerning micropollutant loads have been highlighted for aquatic biota. In one study, Pittura *et al.* (2018) carried out a laboratory study concerning the ecotoxicological effects of benzo(a)pyrene adsorbed on microplastics in *Mytilus galloprovincialis* (blue mussel). The animals were exposed for 4 weeks to polyethylene microplastic, some contaminated with benzo(a)pyrene and others not, at 10 mg L-1 of plastic particles. The molluscs were also subjected to this PAH at 150 ng L-1, equal to non-microplastic adsorption. The study concluded that microplastics act as vectors of this pollutant and that the adsorbed pollutant is transferred to mussel tissues, although the plastic particles did

not induce expressive ecotoxicological effects after 28 days of experiment. Thus, further studies are important to verify long-term damage. Another study assessed the toxic potential of a water reservoir in Feilaixia, on the Beijiang River (China), and found microplastics in all sampling locations, carrying 16 priority types of PAH, suggesting that these pollutants are the result of incomplete fossil fuel combustion. The authors also evaluated the toxic potential of these contaminants, reporting no indication of negative effects on the biota. Furthermore, PAH in drinking water increase the risk not only for the aquatic biota, but also for human health (Tan *et al*., 2019).

Montero *et al.* (2021), in a laboratory study, evaluated the toxicological effects of pollutants (dichlorodiphenyldichlorethylene, chlorpyrifos and benzophenone-3) adsorbed onto microplastics in the diet of marine fish. Young sea bass (*Dicentrarchus labrax*) divided into four groups with different diets, were cultivated and fed for 60 days, receiving pure feed (control group), feed combined with virgin microplastics, feed combined with pollutants and feed combined with associated pollutants and microplastics. The authors indicate that the animals exhibited adequate growth in all diets, doubling their size by the end of the study, but those that received feed containing pollutants adsorbed on microplastics exhibited an inflammatory response in the distal intestine. In addition, both the diet containing pollutants and the one containing pollutants associated with microplastics led to intestinal microbiota changes, reducing beneficial bacteria and increasing pathogenic microorganisms (Proteobacteria and Vibrionales), thus demonstrating the potential of microplastic polljutant absorption to cause intestinal dysbiosis in fish.

Pharmaceuticals

The same patterns reported in previous sections were also observed for pharmaceuticals, such as size, porosity, pH, salinity, ionic strength, electrostatic interactions, hydrogen bonds and hydrophobicity.

In one study conducted in the laboratory, Li *et al.* (2018) analyzed five antibiotics (sulfadiazine, amoxicillin, tetracycline, ciprofloxacin and tretoprim) and their adsorption potential in five types of microplastics (polyethylene, polystyrene, polypropylene, polyamide and polyvinyl) in both water and seawater. The findings report that polyamide exhibited a higher adsorption capacity for antibiotics in freshwater, probably due to microplastic porosity, as well as hydrogen bonds. Adsorption was low in sea water compared to freshwater, while ciprofloxacin and amoxicillin did not eadsorb at detectable levels. The authors conclude that the particularities of each antibiotic will influence this dynamic, in addition to other factors such as pH and ionic forces. In another assessment, Fang *et al*. (2019) observed the adsorption of three types of fungicides (triadimenol, myclobutanil and Hexaconazole) on polystyrene microplastics in a laboratory assessment. In the first 6 hours adsorption rates indicated a rapid increase, followed by a decline until reaching equilibrium after the 24-hour period. The authors indicate that some factors contributed to phenomenon, such as particle size, with smaller particles exhibiting higher adsorption of all three investigated fungicides, although other factors such as pH, ionic, electrostatic and hydrophobic interactions are also important. Atugoda *et al.* (2020), observed the adsorption of the antibiotic ciprofloxacin on polyethylene in the laboratory, reporting that polyethylene particles adsorb this antibiotic in a pH-dependent manner, with maximum adsorption rates at pH 6.5-7.5, as the presence of ionic forces will decrease by 17% in this range. Adsorption was also salinity-dependent, as ciprofloxacin adsorption decreased 89% in no-salt conditions. Another study analyzed contamination levels in waterways of New York observing the adsorption of pharmaceutical products, such as atenolol, sulfamethoxazole and ibuprofen, in other materials (Magadini *et al*., 2020). Virgin microplastic balls of Polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), polyethylene (PE) and polypropylene (PP), in addition to plastic bags (low-density polyethylene – LDPE), PP tube cut into smaller sizes and pieces of glass were used as the control. These materials were inserted throughout the waterways and left for 28 days. At the laboratory, the authors reported high concentrations of atenolol, sulfamethoxazole and ibuprofen in the sampled waters, not surprising given the high volume of treated waste discharged daily in the sampling locations. In addition, the study pointed out that the observed ibuprofen levels negatively affect the development of sea urchin larvae (*Parencendrotus lividus* species) (Aguirre-Martínez *et al.*, 2015).

Other studies have also observed ecotoxicological effects caused by the association of microplastics and pharmaceuticals. Verdú *et al*. (2021), for example, evaluated triclosan sorption and desorption to microplastics and its effects on the cyanobacteria *Anabaena* sp. Low density polyethylene (LDPE), polyamide (PA), polyethylene terephthalate (PET), polyoxymethylene (POM), polypropylene (PP), polystyrene (OS) and biodegradable polylactic acid (PLA) were tested. The authors reported that virgin microplastics did not inhibit cyanobacteria growth, whereas LDPE, PA and POM exhibiting adhered triclosan caused negative growth effects. The authors also observed that the microplastics adsorbed a significant amount of triclosan, enabling the desorption of high concentrations of this pollutant in the environment.

In agreement with the aforementioned study, Gonzalez-Pleiter *et al.* (2021) evaluated the adsorption of the antibiotics azithromycin and clarithromycin on four types of microplastics, namely polyethylene terephthalate (PET), polylactic acid (PLA), polyoxymethylene (POM) and polystyrene (OS). Thet also evaluated the effects of these synthetic polymers, both virgin and adhered to antibiotics, on the cyanobacteria *Anabaena* sp. The two drugs adsorbed to all tested microplastics, but adsorption was higher for azithromycin. Virgin microplastics did not elicit any toxic effects to *Anabaena* sp., whereas microplastics exhibiting adsorbed antibiotics inhibited this cyanobacteria's growth and chlorophyll content. The authors highlighted the harm

caused by microplastic sorption and desorption dynamics of these pollutants, as the investigated cyanobacteria is a primary producers thus affecting the basic trophic level of aquatic ecosystems.

Reviews on microplastic pollutant vector potential

Several reviews on the subject of microplastic pollutant vector potential were also retrieved herein, mainly discussing the factors that influence adsorption dynamics, such as, plastic weathering, type of polymer, environmental pH, salinity, ionic forces, hydrophobicity and adsorbed organic matter (Amelia *et al.*, 2021; Atugoda *et al.*, 2021; Fred-Ahmadu *et al.,* 2020; Hartmann *et al.*, 2017; Kwon *et al.,* 2017; Yu *et al.*, 2019). Other studies addresses potential toxicological damage caused by microplastics in association with microalgae and bacteria (Caruso, 2019), indicating that the micro and nano size of the particles contributes to the dissemination of these harmful microorganisms, causing biological invasions (Shen *et al.*, 2019). In this regard, one study indicated that sorption dynamics in microplastics in ballast water contributed to increase in antibiotic resistance through pathogenic bacteria associated with adsorbed metals, therefore comprising a global health risk (Naik *et al.*, 2019). Another study reviewed the toxic potential of microplastics concerning PAH. reporting that most investigations have focused on the possible carcinogenic effect of this contaminant, although several other harmful effects for humans and animals are noted, such as immunotoxicity, neurotoxicity, reproductive toxicity and endocrine disruption (Souza & Choueri, 2020; Sun *et al.*, 2021). According to Jiménez-Skrzypek *et al.* (2021) contaminants attached to microplastics display increased toxicity, offering biota risks, pointing out that most of the studies focus on persistent organic pollutants and not enough on emerging pollutants. This reinforces the findings reported by by Santana-Vieira *et al.* (2021), that the majority of studies found were regarding PAHs, PCBs, and DDTs, with few studies on pharmaceuticals and personal hygiene products. Still with regard to pharmaceutical products, Santos *et al.,* (2021) discuss that microplastics can present very different dynamics in relation to this contaminant class, as they can decrease, potentiate or even have no effect on certain drugs, as dynamics depend on certain environmental factors, as well as chemical bonds between different types of plastic material. The retrieved reviews also focused on the effects of bioaccumulation. For example, according to Koelmans *et al.* (2016) the effects caused by the ingestion of adsorbed microplastic are within a typical range of equilibrium, presenting risks when exceeding this range. The authors also state that this ingestion can increase the bioaccumulation of some contaminants and at the same time decrease the load of others, so this dynamic must be taken into account in risk assessments. Ziccardi *et al.* (2016) also state that microplastics can increase or decrease the bioaccumulation of hydrophobic organic chemicals, although few studies are available to this end.

Microplastic adsorption interfering factors

Table 1 displays all interfering factors reported in the retrieved assessments for each pollutant class discussed herein. It is interesting to note that light and temperature were not addressed for metals and drugs, as well as the presence of organic and inorganic matter adhered to microplastics, while type of polymeric material and microplastic particle aging were discussed in several studies. For POPs and other chemical pollutants, such as dibutylphthalate, bisphenol A, PCBs and some types of PAH. Hydrophobicity, collection site, size and type of material were the most discussed interfering factors, while the presence of biofilm, organic and inorganic matter adhered, the ratio of sediments compared to microplastics and the degree of toxicity were the least addressed factors. According to Cole *et al.* (2011), POPs dispersed in the aquatic environment can adhere to microplastics and be ingested by animals, transferring this contaminant from the environment to marine organisms. Furthermore, these persistent organic pollutants can be transferred along the food chain, increasing the toxic levels of these contaminants, through biomagnification processes. In this regard, Haratsaris (2018) evaluated the presence of DDTs and PCBs adsorbed to pellets collected on the coast of São Paulo, reporting that the highest concentrations of pollutants adhered to microplastics occurred on beaches where urban and industrial drainages was present, in addition to cargo ships. According to Mendonza and Jones (2015), microplastics are associated with PAH and PCBs as well as in sediment particles, but the microparticles remain on the aquatic surface, facilitating their ingestion by organisms, along with the pollutants, intoxicating the animals that ingest them. In a controlled experiment, DPB demonstrated the ability to desorb from the plastic material of origin and adsorb to microplastics present in water, enhancing the negative effects of these particles for living organisms that mistake these particles for food (Ye *et al.*, 2020). PFAs adhered to plastic particles have been reported in estuarine environments, demonstrating possible toxic potential for biota (Cheng *et al.,* 2021). All evaluated drugs displayed some degree of microplastic adsorption, both in salt water and in fresh water (Li *et al*., 2018).

Table 1. Microplastic adsorption interfering factors for each pollutant class discussed in the present study.

	REFERENCE	POLLUTANTS Aged particle	INTERFERING FACTORS												
			Presence of biofilm	Organic/inorganic matter	Collection place	Type of material	Material size	pH	Eletrostatic/ionic forces	Salinity	Light	Temperature	Hydrophobicity	Toxicity	Sediment X microplastic
Metals	Turner and Holmes (2015)	Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn	x	x					x						
	Foshtomi *et al*. (2019)	Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Ti, Zn													x
	Selvam *et al.*(2021)	As, Cd, Cr, Cu, Pb, Mn, Zn					x								
	Sarkar *et al*. (2021)	As, Cd, Cr, Cu, Ni, Pb, Zn				x	x							x	
	Carbery *et al*. (2020)	As, Ba, Cr, Cu, Mn, Pb, Se, Zn	x			x									
	Wang *et al*. (2020)	Cd												x	
	Godoy *et al.* (2019)	Cd, Co, Cr, Cu, Ni, Pb, Zn		x					x		x				
	Besson *et al*. (2020)	Cd, Cs, Zn	x	x											x
	Guan *et al*. (2020)	Ag, Cd, Co, Cu, Ni, Zn	x	x											x
	Brennecke *et al.* (2016)	Cu, Zn	x												
	Ta and Babel (2020)	Cr, Cu, Ni, Pb	x				x								x
	Purwiyanto *et al.* (2020)	Cu, Pb					x		x		x				
	Gao *et al.* (2019)	Cu, Cd, Pb	x				x	x							

	Pittura *et al.* (2018)	PAH													x	
	Foshtomi *et al.* (2019)	PAHs, TPH														
	Wu *et al.* (2019)	Bisphenol						x	x				x			
	Ye *et al.* (2020)	DBP									x	x				
	Wang Z. *et al.* (2018)	Phenanthrene and phenol	x			x	x						x			
	Tan *et al.* (2019)	PAH			x	x									x	
	Tang *et al.* (2018)	PAH (3- and 4-ringed and alkylated PAHs)			x											
Persistent Organic Pollutants and others	Lončarski *et al.* (2021)	PAH	x			x	x						x			
	Frias *et al.* (2010)	PAH, PCBs, DDT			x	x										
	Chen *et al.* (2020)	PAH				x	x									
	Mendoza and Jones (2015)	PAH, PCBs			x	x	x									x
	Liu *et al.* (2016)	PAH					x									
	Noro and Yabuki (2021)	PAH									x	x				
	Bouhroum *et al*. (2019)	PAH, PCBs			x											
	Yu *et al.* (2020)	PAH	x						x				x			
	Wang *et al.* (2020)	Pesticides	x								x	x	x			
	Cheng *et al.* (2021)	PFAs			x	x		x		x		x				
	Llorca *et al.* (2018)	PFAs, carboxylic acids, sulfonates, sulfonamide	x			x	x	x	x							
	Li *et al.* (2020)	POPs						x					x			
	Scott *et al.* (2021)	PFAS		x	x											
	Li *et al.* (2018)	Antibiotics				x		x	x	x						
Pharmaceuticals	Atugoda *et al.* (2020)	Antibiotics						x	x	x						
	Magadini *et al.* (2020)	Antibiotics	x	x	x	x									x	
	Fang *et al.* (2019)	Triazole fungicides					x	x	x				x			

CONCLUSIONS

The present study discussed microplastic potential to act as a transport agent for different chemical pollutants through interactions that depend on several environmental factors, such as salinity, light, temperature, pH, as well as microplastic characteristics, such as type of material, age, and the presence of adhered biofilm and organic matter. Although microplastics assessments in the literature are almost 2 decades old, few studies on their relationship with chemical pollutants are available to date, indicating a knowledge gap in this regard. Furthermore, bibliographic searches only in Portuguese retrieved very limited results, indicating scarce assessments disseminated in this language.

AUTHOR CONTRIBUTIONS

MRG: Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. JVP: Data curation, Formal analysis, Writing – review & editing. RAHD: Supervision, Conceptualization, Resources, Data curation, Writing – original draft, Writing – review & editing. All authors contributed intellectually to the manuscript.

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