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Microplastics and associated emerging contaminants in the environment: Analysis, sorption mechanisms and effects of co-exposure

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A B S T R A C T

Microplastics (MPs) and other emerging pollutants exist together in the environment and their co-exposure represents a source of increasing concern as MPs have been reported to act as carriers of pollutants due to their high sorption capacity. The ingestion of contaminated MPs by organisms can enhance the desorption of pollutants, increasing their bioavailability and toxicity. This review examines the role of MPs as vectors of environmental emerging contaminants. First, the main tools used to identify and characterise MPs and the analytical methods used for the determination of associated emerging contaminants are discussed. Insightful explanations of the sorption interaction between several groups of emerging pollutants and MPs are provided. MP type (polarity, crystallinity, size) and aging process together with the environmental conditions and pollutant properties (hydrophobicity and dissociated forms) are key factors influencing the sorption process. The literature review showed that polyethylene and polystyrene were the most commonly studied polymers. Antibiotics, perfluoroalkyl compounds and triclosan showed high sorption capacities onto MPs. Finally, the effect of co-exposure to MPs-emerging pollutants and bioaccumulation in aquatic and terrestrial organisms is discussed. The combined exposure may impact the toxic effects in different ways, through synergistic or antagonic interactions. Examples of different scenarios are provided, but in general the research conducted on terrestrial systems is scarce. The results revealed a lack of standardization in laboratory studies and in the testing conditions that reflect actual environmental exposure.

1. Introduction

Plastics are used in many day-to-day applications [1]. Recent data show that of the 320 Mt of plastics produced globally each year, 94% will accumulate in the environment [2]. Microplastics (MPs) are polymeric particles ranging from 100 nm to < 5 mm in diameter. The main sources of primary MPs are laundering of synthetic clothes, pharmaceuticals and cosmetic products like facial scrubs, and pellets and abrasive components used to clean industrial machinery. MPs are released into the environment through: i) direct discharge of plastic waste into water bodies, ii) discharge from industrial and domestic wastewater treatment plants (WWTPs), and iii) plastic waste in fishing vessels, fisheries, and water operation industries [1]. In the environment, secondary MPs are originated from the degradation of larger plastic items like fishing nets or plastic bags to smaller ones due to weathering [3].

MP polymers have been found everywhere: in water bodies, land and air [1–4]. The most commonly found MPs are polyethylene (PE) and polystyrene (PS) followed by polypropylene (PP), polyvinylchloride (PVC), polyethylene terephthalate (PET), polyamide (PA) and polyvinyl alcohol (PVA) [4]. Due to the slow degradation rate of MPs, they accumulate and persist for long periods of time in the environment where they can interact with organisms. In this regard, there has been abundant research on MP-related issues including their source, fate and interaction between MPs and different aquatic constituents (i.e. planktons, aquatic plants, invertebrates, fish, and water birds) [4,5].

Additionally, MPs coexist with mixtures of contaminants in the environment and have been reported to act as vectors for the transfer of these chemical contaminants from water and soil to aquatic and terrestrial organisms. This usually occurs via the sorption of organic pollutants on the hydrophobic surface of the MPs. The chemical pollutants that interact with MPs can be classified into two groups: a) additives added to plastics to achieve the desired physical and chemical properties (antimicrobial [triclosan], thermoresistance [polybrominated diphenyl ethers], antioxidant [nonylphenol]); and b) chemicals adsorbed from the surrounding media [4,6]. Pharmaceuticals,

personal care, household and industrial products, such as antibiotics, preservatives, UV filters, flame retardants or perfluoroalkyl substances (PFASs), are emerging pollutants of particular concern. These products are continuously released into the environment in large amounts and their ecological concern is associated with their persistence, bio-accumulation capacity, and limited removal rate at WWTPs [1,4].

Aquatic organisms can be exposed to high concentrations of pollutants through ingestion of contaminated MPs. In this regard, it has been reported that the concentration of contaminants on MPs could be several orders of magnitude higher than in the surrounding water. For example, MPs were found to have polychlorinated bisphenyls (PCBs) in concentrations 10^5-10^6 times higher than in the surrounding seawater [6]. This combination (MP-emerging pollutant) represents a serious environmental concern as they may change the environmental fate, bioavailability and biomagnification of environmental contaminants [1,4]. Recent studies have shown that after ingestion by marine organisms, their digestive fluids promote the desorption of the adsorbed contaminants and the assimilation into their body tissues [7]. However, the uptake of emerging pollutants adsorbed on MP particles has been scarcely studied and questions regarding the influence of the different components of the mixture remain unanswered. Recent studies on pollutant bioaccumulation in aquatic species have shown that combined exposure is associated with both synergistic [8,9] and antagonistic [10, 11] effects. However, the implication of MPs as carriers of pollutans to biota relative to other exposure routes is still largely unkwnown.

The study of MPs-associated emerging pollutants is a rapidly evolving field with a growing number of publications. Although some emerging pollutants such as antibiotics or the antimicrobial triclosan have been investigated extensively, comprehensive reviews including other families of pharmaceuticals, personal care and household products are lacking. This work provides a comprehensive overview on this topic that includes i) the analytical tools used to characterize MPs and to extract and determine associated emerging pollutants; ii) sorption mechanism and significant factors influencing this process; iii) co-exposure potential effects and bioaccumulation in the aquatic and terrestrial biota; and iv) bioaccesibility/bioavailability of MPs-associated emerging pollutants, with more than 119 papers included.

2. Analytical tools for the analysis

2.1. Identification and characterization of microplastics

Different techniques need to be applied to study MPs in environmental matrices. The detection and characterization of MPs typically involve three steps:

1) Separation and extraction: Separation of MPs is normally done using sieves with individual or in series mesh (0.038–4.75 mm) or filters of small mesh sizes (0.02–5 μm). For MPs < 1 μm, active and passive separation techniques are applied such as field flow-fractionation (separation is achieved by applying an external field into micro-fluidic samples and it can be applied to high molar mass polymers, proteins, and nanoparticles) and hydrodynamic chromatography (separation is achieved by applying hydrodynamic and surface forces and it can be applied to particles from 10 nm to 1000 nm in size), respectively [12]. Solid environmental samples (sewage sludge, sediment or biota) differ from water samples at the first separation step. For the former, separation methods such as the electro-separator, the Munich or MicroPlastic Sediment Separator (MPSS) are proposed [13]. Electro-separation is a fast method for larger samples that involves the use of smaller volumes of chemicals. MPSS also separates plastics from larger samples but needs larger amounts of $ZnCl_2$. For the removal of the high content of organic matter present in environmental samples (except for sediments processed with MPSS) an alkaline digestion with KOH, oxidizing digestion with H_2O_2 or enzymatic digestion are usually used since these processes does not or only slightly degrade polymers. Additionally, a density separation is conducted in many studies to separate MPs from sediments or other inorganic matter, which is not removed during the digestion process. For density separation, a high concentrated or even saturated salt solution is mixed with the sample and shaken. In general, a heavy liquid solution with higher density than plastics such as NaCl, NaI, $ZnCl_2$, HCO_2K, $H_4Na_2O_6W$, canola oil or an elutriation column should be used [13].

2) Visualization and Quantification: A light microscope or the naked eye are used for identification of larger particles of MPs (1–5 mm). The assessment of the light transmission, color, and shape allows us to distinguish plastic from non-plastic particles. For small MPs (< 1 mm) scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) is used for morphology characterization and determination of the elemental composition. SEM allows us to differentiate plastic from plastic-like particles. Other techniques such as fluorescence microscopy or flow cytometry are also applied for visualization [12].

   Dynamic light scattering and measurements of zeta potentials are usually used for the determination of surface charge and hydrodynamic size and fluorescence spectroscopy is used for assessing the toxicity of pollutants and the harmful effects of MPs on organisms in soil or water, such as changes in the enzymatic regulation. Atomic force microscopy (AFM) and hybrid AFM techniques have emerged as powerful tools for MP characterization as they can be used for the assessment of surface morphology, stiffness, adhesiveness, hydrophobicity, conductivity, magnetization, and work function.

3) Chemical identification: Raman spectroscopy is a highly reliable mapping technique for the chemical identification of MPs in both solid and liquid samples, but the presence of adsorbed contaminants or additives, color, and fluorescence might interfere with Raman analysis. Fourier transform infrared (FTIR) spectroscopy is a complementary technique for Raman spectroscopy which has been widely used for MP and adsorbed pollutant identification in environmental samples (it can identify the functional groups of the pollutants adsorbed on the MPs after adsorption assays). Cincinelli et al. [14] used FTIR combined with microscopy to determine the extent of MP contamination in seawater with high spatial resolutions. The main disadvantage of FTIR is that dry samples need to be ground to fine powder to reduce particle size. In addition, mass spectrometry-based methods such as GC–MS coupled with different techniques like sequential pyrolysis (Pyr-GC/MS) and thermal desorption pyrolysis (TD-Pyr- GC/MS) has also been used for MP characterization.

2.2. Determination of associated emerging pollutants in miscroplastics

Recent works [12,15,16] have exhaustively reviewed the main techniques used for sampling, identification and quantification of MPs in freshwater and marine compartments. In general, these reviews highlight the need for standardized experimental procedures in relation to the complex changes, cross-contamination and different properties of MPs associated with particle size and chemical composition [12].

On the other hand, despite the new methods developed for emerging pollutant determinantion in environmental matrices, additional research is required to adapt the available methods to MP matrices in order to provide robust and reliable data about their environmental co-occurrence and fate [16]. One of the main difficulties in MP characterization is the high heterogeneity in shape, size, and chemical composition of MPs that can be found in the same sample, especially in samples exposed to the marine environment. In a recent work, Santana-Viera et al. [16] have reviewed the analytical methods used in the extraction and determination of organic compounds adsorbed onto MPs and concluded that there is a the lack of information regarding the procedures applied in some of the reviewed papers. Many authors have relied on procedures developed for other matrices given the lack of specific

analytical methods for MPs [16]. Conventional liquid–solid extraction techniques have been normally preferred, but others such as ultrasound solvent extraction (USE) and accelerated solvent extraction (ACE) are also being used. Newer extraction techniques, such as supercritical fluid extraction, have not yet been used for MP extraction. Rani et al. [17] used USE with dichloromethane for the extraction of UV filters and antioxidants from several MPs (PE, PP, PET, polycarbonate (PC) and acrylic/styrene) with recoveries between 70% and 116%. Llorca et al. [18] utilized USE with methanol for the extraction of PAFSs in plastic pellets with recovering rates between 50% and 126%.

The main difficulty is the lack of identical laboratory pellets, in terms of size and weight, used for spiking. Methods developed for the determination of pollutants adsorbed onto plastic pellets might not be suitable for determinations in MP fibers with different sizes, characteristics and composition. Lastly, most of the available studies focus on heavy metals and highly hydrophobic contaminants, but there is a lack of research on contaminants of emerging concern (such as personal care products and pharmaceuticals) as well as on methods developed for the determination of these chemicals in soil.

3. Factors influencing sorption processes

The main factors affecting the sorption of emerging pollutants onto MPs can be divided into three categories (Fig. 1): 1) MP type such as polarity, crystallinity and size as well as MP aging; 2) Physico-chemical properties of the pollutants such as hydrophobicity and pKa; 3) Environmental conditions such as salinity, temperature, pH and dissolved organic matter (DOM). Table 1 [19–49] summarizes the laboratory studies that have investigated the sorption of a wide group of emerging pollutants onto virgin and aged MPs with their estimated maximum adsorption capacities, kinetics and mechanisms. Out of the 31 selected studies, 16 focus on pharmaceuticals, specifically on antibiotics (68%), followed by the antimicrobial triclosan and PFASs. As shown in Table 1, PE (n = 21) was the most commonly polymer studied in laboratory experiments followed by PS (n = 16), PVC (n = 11) and PP, (n = 11), PA (n = 4), PLA (n = 3), and PET (n = 2).

3.1. Effects of the physicochemical properties of microplastics

3.1.1. Polarity of MPs

The functional groups and polarity of MPs (Table 1) play a major role in the adsorption capacity [3,50–52]. PS, PP and PE are typically non-polar plastics, while PVC, PET and PA are polar, in particular the latter, which is considered strongly polar. Generally, those organic compounds having high LogKow (>3) values are likely to be absorbed by MPs more easily through hydrophobic interactions. O' Connor et al. [52] reviewed the preferential partitioning of persistent chemicals (Kow 2–8) on MPs and concluded that high density PE (HDPE) and low-density PE (LDPE) show higher partitioning than PP > PVC > PS. Hydrophobic interactions governed the partition mechanism of antibiotics [19,25–27], beta-blockers [26,29], anti-inflammatory drugs [28], lipid regulators [32], PFASs [41–43] and phthalates [51] onto MPs such as PS, PE or PP. However, unlike other hydrophobic contaminants, many pharmaceuticals and personal care products present hydrophilic and polar groups in their structure, which indicates that other factors in addition to hydrophobic interactions such as pore filling, electrostatic, hydrogen and π-π bond interactions are involved (Table 1). Due to specific MPs/pollutants interaction, no rule can help predict the sorption mechanism. For example, it has been reported that the sorption of sulfamethoxazole and sulfamethazine to PE is lower than sorption to glassy PA, a strongly polar polymer [53]. Several authors have concluded that the increased sorption capacity of PA for antibiotics is related to its porous structure and complex hydrogen bonds attributed to the formation of hydrogen bonds between the amide groups (proton donor groups) in PA and carbonyl groups (proton acceptor groups) present in antibiotic structures [1]. Similar results have been found for BPA [39]. Li et al. [20] found that antibiotics are strongly adsorbed to PA, followed by PE, and showing less interaction with PVC.

3.1.2. Crystallinity

Another characteristic of MPs that influences the sorption process is the degree of polymer crystallization. MP polymers show different structures with amorphous and crystalline regions. The amorphous region is made of long chains arranged irregularly and the crystalline part is made of chains bound in a regular geometric lattice (order size of 1 μm) [4,50]. It seems that hydrophobic pollutants can more easily get into the amorphous regions, where the free volume and void areas increase between the polymeric chains [4,50].

3.1.3. Size of MPs

Another factor that influences the sorption capacity is polymer size. In this regard nanoplastics (NPs) have been found to exchange pollutants at higher rates than MPs, which seems to be related to higher surface areas and direct proximity to polymers. Arienzo et al. [4] reported a sorption rate two-fold higher for NPs than for MPs. Ma et al. [36] indicated that PVC particles of small size (<1 μm) have greater K_d values

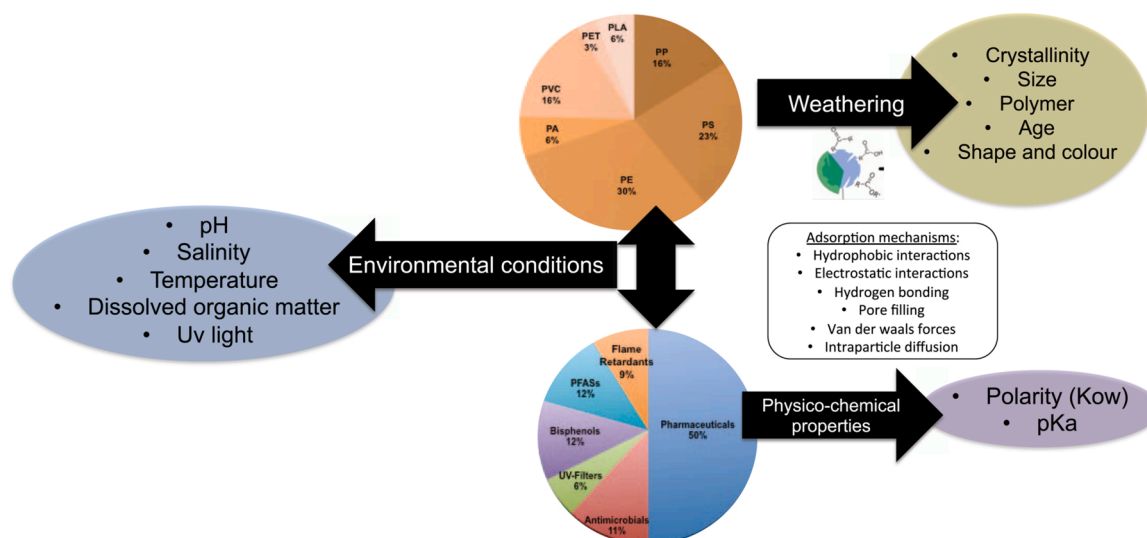**Fig. 1.** Factors governing the sorption of emerging pollutants by MPs.

Table 1

Sorption studies of emerging pollutants onto MPs.

MP		Chemical group	Variables tested	MP (mg) /Water (mL)	Concentration range (mg/L)	Equilibrium time (h)	Adsorption mechanism				Characterization techniques	Reference
Type	Size (μm)						Isotherm model	qmax	Kinetic model	Type of intercation		
PE, PS, **PA**, PP, PVC	75–180	Sulfadiazine, amoxicillin, tetracycline, ciprofloxacin, trimethoprim	Freshwater and seawater systems	20/5	0.5–15	4 d	Linear	Kd: 7.36–756 L/ kg	–	Porous structure and hydrogen bonding	SEM, XRD	[20]
PE	100	Ciprofloxacin	pH, salinity and DOM	2000/ 1000	30–500	12	Hill and Dubinin–Radushkevich	5.82–6.05 mg/g	Parabolic diffusion and Elovich	Hydrophobic and electrostatic interactions	SEM, FTIR	[19]
PS	450–1000	Oxytetracycline	pH, salinity and DOM	50/30	2.0–50	54	Freundlich	27.5 mg/g	–	Electrostatic interaction, H-bonding and multivalent cationic bridging	FTIR, SEM, Specific Surface Area, potential Z	[21]
PLA, PVC	250–550	Tetracycline and ciprofloxacin	Aging and desorption	20/50	5.00	48	Freundlich	0.96–5.49 mg/g	Pseudo-second-order	Hydrogen, π-π bonding and electrostatic interactions	FTIR, XPS, Zeta potential and Specific Surface Area	[22]
PE	150–425	Tetracycline, chlortetracycline, oxytetracycline	pH and salinity	250/30	0–50	30	Freundlich	53–64 μg/g	Pseudo-second-order	Non-bond interactions	FTIR, XPS, SEM	[23]
PLE, **PLA**, POM, PS	3000–5000	Azithromycin, clarithromycin	Desorption and effect on cyanobacterium	1000/20	0.1–10	24	–	1.78–2.70 μg/g 0.94–2.98 μg/g	–	Hydrophobic interactions	–	[24]
PLE, **PLA**, PP	100–150	Sulfamethoxazole	Aging, pH, salinity and DOM	40/20	0,5–10	24	Langmuir and Freundlich	0048–0167 mg/ g	First-order kinetic model and pseudo-second-order	Hydrophobic interaction or electrostatic interaction		[25]
PP, **PE**, PVC	powders	Enrofloxacin, ciprofloxacin, norfloxacin, 5-fluorouracil, methotrexate, flubendazole, fenbendazole, propranolol, nadolol	pH and salinity	100/1	0.5	24	Linear	Kd: 0.2–2.4 L/ kg	–	Hydrophobic and electrostatic interactions	Specific Surface Area	[26]
PP	500	Sulfathiazole, sulfamerazine, sulfamethazine, sulfamethoxazole, ciprofloxacin, enrofloxacin, ofloxacin, norfloxacin, tetracycline, chloramphenicol, venlafaxine	Aging	100/200	5.0–40	72	Langmuir	0.33–2.55 mg/g	Pseudo-second-order	Hydrophobic and hydrogen bonding interaction for fresh PP and electrostatic interaction and hydrogen bonding for aged	SEM-EDS, Specific Surface Area, FTIR, and XPS	[27]
PE, PET, PP, PS, PVC	< 5000	amoxicillin, atrazine, diuron, paracetamol, phenol and vancomycin	pH and temperature	100/100	1	121–28 d	Langmuir	4.0–8.80 mg/g	Pseudo-second-order	Electrostatic interactions	–	[28]
PE	45–48	Sulfamethoxazole, propranolol, sertraline	–	8.0/40	0.001–0.1	96	Linear and Freundlich	46.09, 64.38, and 88.80 μg/g	Pseudo-second-order	Hydrophobicity and electrostatic interactions	SEM	[29]
PS, **PE**, PP	300–1000	Ibuprofen, naproxen, diclofenac	pH and synthetic seawater	600/60	0.05–0.55	48	Linear	Kd: 2–32 L/kg	–	Hydrophobic interactions	XRD, SEM, DSC,	[30]
PE	0.5–1	Diclofenac	pH, salinity and MP size	20/30	10–1000	24	Langmuir and Freundlich	0.25–0.46 mg/g	Pseudo-second-order	Hydrophobic and electrostatic interactions	FTIR, SEM	[31]
PS	50	Atorvastatin and amlodipine	Aging and derivates	5 g/L	1	48	Langmuir and Freundlich	0.2–1.4 mg/g		Hydrophobic and π-π interaction	XRD, XPS, SEM, FTIR	[32]

Table 1 (*continued*)

MP Type	Size (μm)	Chemical group	Variables tested	MP (mg)/Water (mL)	Concentration range (mg/L)	Equilibrium time (h)	Adsorption mechanism Isotherm model	qmax	Kinetic model	Type of intercation	Characterization techniques	Reference
									Pseudo-second-order			
PE	250–280	Carbamazepine, 4-methylbenzylidene camphor, triclosan, 17α-ethinylestradiol	Salinity and DOM	10/50	0.01–0.2	5 d	Linear	Kd: 51–311 L/kg	–	–	–	[33]
PS, PVC	0.04 and 1–74	Ciprofloxacin, BPA	Aging, pH, DOM, salinity and cations	10/20	2.0–50		Linear	0.15–8.71 mg/g	–	Hydrophobic, π-π stacking, electrostatic interaction and hydrogen bonding	XRD, SEM, FTIR	[34]
PE, PS	225–313	Triclosan	Desorption and soil	40/20	1.8–11 mg/L	96	Temkin	1248 μg/g (PE) 1033 μg/g (PS)	Pseudo-second-order	–	SEM, Specific Surface Area and Zeta potential	[35]
PVC	< 1–74	Triclosan	pH and salinity	10/25	2.0–20	24	Dubinin–Radushkevich	8.98–12.7 mg/g	Pseudo-second-order	Liquid-film and intra-particle diffusion, hydrophobic and electrostatic interactions, halogen and hydrogen bonding	XRD, XPS, SEM, FTIR	[36]
PP	< 180	Triclosan	pH and salinity and aging	20/20	0.1–10	96	Freundlich	2–6 mg/g	Pseudo-first-order	Electrostatic interaction	FTIR, SEM, XRD, XPS, TG-DSC	[37]
PVC	< 13.2	BPA, BPS, BPF, BPB, BPAF	–	1.5 g/L	0.1–1	18	Freundlich	0.16–0.24 mg/g	Pseudo-second-order	Hydrophobic, electrostatic forces, and noncovalent bonds	–	[38]
PE, PP, PS, PC, PVC, **PA**, PMMA, PE, PU	–	BPA	Salinity, pH, coexisting estrogens, and water chemistry	500/20	0.001–0.5	3d	Freundlich	Kd: 0.41–76 L/kg	–	Hydrophobic and π-π interactions, hydrogen bonding	Specific Surface Area, DSC	[39]
PVC, PE	–	BPA	Aging, salinity, coexisting polluatnts, desorption and water chemistry	1000/40	0.05–0.5	360	Linear	Kd: 7.6–22.2 L/kg	Pseudo-second-order	Pore-filling and hydrophobic interaction	Specific surface area	[40]
PE	4–500	PFOS	Size and desorption	25/500	0.05–600 μg/L	7 d	Linear		Linear	Hydrophobic interactions	–	[41]
PE, **PP**, PES, PA	2000–3000	PFOS	Desorption	5000/1000	0.005–01	3 d	Freundlich and linear	1.12–2.02 μg/g	Pseudo-second-order	Hydrophobic interactions and hydrogen bonding. Presence of polarized N − H bonds	SEM, FTIR, Specific Surface Area, EDS	[42]
PE, PS, PVC	150–230	PFOS, FOSA	pH and salinity	100/20	0.005–50	7 d	Linear	Kd: 32–298 L/kg	–	Hydrophobic interactions	–	[43]
PE, PP, PET, PA, PLA, Styrene, ABS, tyre	< 500	PFOA, PFOS	Real MPs, lake water	30/20	1500	14 d	–	–	–	Hydrophobic and Van der Waals interactions	SEM, FTIR, Specific Surface Area, XRD	[44]
PS, PE	< 5000	18 PFASs (carboxylic acids, sulphonates and sulphonamide)		2.0–5.0 mg/L	0.001–0.02	7 d	Linear	Kd: 4–4240 L/kg	–	Salting-out, hydrophobic, electrostatic and Van der Waals interactions	–	[45]
PE, PS	250–300	BP-3, 4-MBC	Multi-solute systems and desorption	10/25	0.02–0.2	48	Linear	log Kd: 2.52–2.19 L/kg 4.15–2.82 L/kg	–	π-π interactions	–	[46]
PE, PVC	125–1000			20/25	0.001–0.005	24		443–1246 ng/g		Pore-filling	FTIR	[47]

Table 1 (*continued*)

Type	Size (μm)	Chemical group	Variables tested	MP (mg)/Water (mL)	Concentration range (mg/L)	Equilibrium time (h)	Isotherm model	Kinetic model	qmax	Type of interaction	Characterization techniques	Reference
		tri-n-butyl phosphate and tris (2-chloroethyl) phosphate	MP size and temperature				Freundlich and Langmuir	first-order kinetic model and pseudo-second-order				
PE, PP, **PS**, PA	4000	Polybrominated diphenyl ethers (BDE-47, BDE-99, BDE-153)	pH, salinity and DOM	500/30	0.03–226 ng/L	24	Freundlich	Pseudo-second-order	6.41–14.42 ng/g	–	SEM, FTIR, Specific Surface Area, XRD, TG-DSC	[48]
PE, PP, PS, **PVC**	150	Tetrabromobisphenol A	pH, salinity and DOM	20/-	0.005–100	48	Intraparticle diffusion	Pseudo-second-order	PVC (101.85 mg/kg) >PS (78.95 mg/kg) >PP (58.57 mg/kg) >PE (49.43 mg/kg)	Hydrophobic and electrostatic interactions	SEM, FTIR, Specific Surface Area	[49]

MP with the best adsorption capacities is marked in bold. Acronyms: ABS: Acrylonitrile butadiene styrene; EDS: energy dispersive spectroscopy; FTIR: Fourier-Transform Infrared Spectroscopy; SEM: Scanning Electron Microscope; PE: Polyethylene; PC:Polycarbonate; PMMA: Polymethylmethacrylate; PP: Polypropylene; PS: Polystyrene; PA: Polyamide; PET: Polyethylene terephthalate; PLA: Polylactic acid; POM: Polyoxymethylene; PU: Polyurethane; TG-DSC: Thermogravimetry and differential scanning calorimetry; XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy.

for triclosan (1.35 L/g > 1.05 L/g) and greater adsorption capacity (12.7 mg/g > 8.98 mg/g) than PVC particles of larger size (about 74 μm), which is also related to the higher surface area, hydrophobicity and relatively small electronegativity of small size particles.

3.1.4. Aged MPs

Weathering degradation leads to changes in polarity and, therefore, in the sorption capacity of MP particles [4,54–57]. The formation of new end groups, especially carbonyl, hydroperoxides and ketones results in a shift from hydrophobic to hydrophilic surfaces and a decreased retention of organic pollutants [55]. In addition, oxidation induces chain scission and a predominance of the amorphous region which in turn increases diffusion and sorption of organic pollutants [3,54]. In this regard, Ding et al. [54] showed that the adsorption capacities to PS of antibiotics and PAHs were influenced by the degree of weathering as weathering led to increased surface area and increased formation of oxygen-containing functional groups. This results in strong sorption of antibiotics to PS, but in weak sorption of PAH because the oxygen-containing functional groups easily form hydrogen bonds with the surrounding water molecules. Similar results were reported by Kong et al. [25] for sulfamethoxazole using PLA, PET and PP artificially aged by thermal activation. As the aging time increased, the adsorption capacity also increased significantly [from 0.276 to 0.479 mg/g for PLA, and from 0.048 to 0.132 mg/g for PET and from 0.053 to 0.167 mg/g for PP, pristine and at 20 days, respectively]. Using simulations based on density functional theory, Shih et al. [55] described the formation of hydrogen bonding between the camphor part of the UV filter 4-methyl-benzylidene camphor (bond acceptor) and RCOOH moieties (bond donor) of aged PET. In their experiments, the authors described an increase from 5 to 11 mg/g in the sorption capacity only after a 5-day aging. Liu et al. [32] described different adsorption mechanisms to virgin and aged PS for the pharmaceuticals atorvastatin and amlodipine. The adsorption on virgin PS was related to hydrophobic and π-π interactions, but as PS ages, adsorption was related to hydrogen bonding and electrostatic interactions. In another work by Liu et al. [57], the sorption capacities of UV-weathered PS and PVC for ciprofloxacin were found to be respectively, 120% and 20% higher than the virgin plastics. Cation exchange, electrostatic interaction, hydrogen bonding, and π-π interaction were the main sorption mechanisms. Bhagwat et al. [42] revealed that biomass accumulation on aged MPs led to higher surface areas compared to virgin MPs; accordingly, the detected concentrations of adsorbed PFOS were 20 − 85% higher in aged MPs and were different depending on the MP type (PP>PE>PA>PS).

3.2. Effects of the emerging polluatnts properties

As mentioned above, affinity in terms of similar hydrophobicity is a key factor governing sorption [4,33,43]. For example, the less polar, non-ionic perfluorooctanesulfonamide (FOSA) showed increased partitioning to PE and polar perfluorooctanesulfonate (PFOS) showed increased partitioning to PVC and decreased partitioning to PS [43]. Wu et al. [33] reported that the partitioning of 4-methyl benzylidene camphor, carbamazepine, 17α-ethinylestradiol, and triclosan on PE was linear and correlated with their distribution coefficient (K_d) values (between 191 and 53,225 L/kg for carbamazepine and 4-methyl benzylidene camphor, respectively, which is consistent with their hydrophobicities).

The adsorption capacity of MPs can also vary between the dissociated forms of pollutants. When the solution pH exceeds the zero point of charge (pHpzc) of MPs, their surface will be negatively charged and atract positively-charged pollutants through electrostatic interaction. When the pH of the environment exceeds the pKa of the pollutants, they will be deprotonated in an anionic form, causing electrostatic repulsion and decreasing the adsorption by MPs. For example, Zhang et al. [21] found higher adsorption capacities at pH = 5 when oxytetracycline is almost entirely in its zwitterionic form (3.27–7.32) and the surface

charge of PS approaches the pHpzc (4.96). This results in the lowest electrostatic repulsion between oxytetracycline and PS, indicating that electrostatic interaction may have regulated adsorption. Li et al. [20] showed that ciprofloxacin (a cationic antibiotic found in water systems) has a higher adsorption capacity onto MPs than other antibiotics such as sulfadiazine, tetracycline or trimethoprim, which exist in zwitterionic and anionic forms in water environmental systems. Elizalde-Velázquez et al. [30] studied the sorption of naproxen, ibuprofen and diclofenac to PE, PP and PS particles in environmental conditions and found that PE showed the highest affinity for the three chemicals. The authors also described how pH can affect the sorption mechanisms through changes in the surface charge of MPs and speciation of the drugs. Increased sorption of the three studied pharmaceuticals to MPs was observed under acidic conditions, a process regulated by hydrophobic interactions.

3.3. Effects of environmental factors

3.3.1. Salinity
Increased salinity has been reported to increase MP aggregation, and therefore the number of sorption sites, as well as to enhance water solubility of organic chemicals [4,57]. Liu et al. [57] observed that chlorine present in PVC increases the cohesion between polymer chains, which in turn decreases the free volume available for the diffusion of ciprofloxacin. In contrast, Na present in PS saturates its surface preventing electrostatic interactions with positively charged ciprofloxacin at pH < 6.0.

3.3.2. Temperature and DOM
In general, high temperature and high content of DOM decrease sorption to MPs through competition with pollutants to bind to sorption sites and complexation with the hydrophobic parts of humic and fulvic acids, which modifies the partitioning between the solid surface and water [4,19]. Increases in the concentration of fulmic acid of 20 mg/L led to a marked decrease in the sorption of tetracycline on PS, PP, and PE (93%, 95%, and 97%, respectively) [58]. Similarly, Wu et al. [33] reported that an increase in the concentration of fulmic acid of 20 mg/L resulted in decreased sorption capacity of PE for triclosan, 17 α-ethinylestradiol, and 4-methylbenzylidene camphor; however, this increase of fulmic acid did not seem to affect carbamazepine sorption. Xu et al. [58] and Liu et al. [51] found that DOM does not affect the sorption of sulfamethoxazole and phthalate compounds on MPs, while other studies have found contradictory results. Chen et al. [59] described the formation of a copolymer, DOM-MPs, by the interaction between the aromatic structure of some MPs and the carbonyl functional groups of DOM. As this copolymer shows high electron density, it binds to positively charged molecular species.

3.3.3. pH
pH is another important factor influencing sorption mechanisms as changes in pH can lead to speciation of pollutants and changes in the surface charge of MP particles. As mentioned above, NSAIDs are strongly sorbed to MPs only in acidic conditions (pH 2) MPs [30]. Liu et al. [57] investigated the interactions between ciprofloxacin (cation at pH < 5.0, anion at pH > 10.0, and zwitterionic at pH 7.0) and PVC and PS and found that at pH < 6.0 the sorption mechanism between the positive charge of ciprofloxacin and the negative charge on the MP surface occurred through electrostatic interactions. At pH > 9.0 electrostatic repulsion occurs and consequently the adsorption decreases.

Thus far, research has been mainly done in laboratory settings. However, in spite of providing information regarding sorption mechanisms, laboratory experiments cannot replicate the complex interactions between MPs and pollutants that occur in aquatic environments. In addition, there is no consensus regarding the set of experimental conditions or the variables to be investigated in the actual environment [44]. In this sense, Ateia et al. [44] compared the adsorption behavior of

a pesticide, a pharmaceutical and three PFASs onto crushed plastics to recreate 'real interactions' with virgin polymers. Pure MPs had a lower uptake values than real MPs in most cases explained by the surface roughness and/or the presence of fillers of real samples. Additionally, given the high complexity of the interactions occurring in the different environmental compartments, research should include multiple coexisting pollutants.

4. Co-exposure to microplastics and emerging pollutants

The simultaneous study of MPs and emerging pollutants is mandatory and a topic of environmental concern since their combination could lead to changes in their environmental fate, bioavailability and biomagnification, which might pose an additional threat to living organisms [1,7,60,61]. Researchers have started to study and compare the effects of single versus combined exposure on biota. Table 2 [8–11,24, 35,62–84] provides a summary of the studies carried out under labarotary conditions on aquatic and terrestrial organisms. Data such as species, concentration and type of tested polymer, concentration and type of the emerging pollutant, experimental design, as well as comments on the results are included. A high number of studies found synergistic effects related to coexposure to MPs and emerging pollutants, while other studies found that this synergistic effect was rather insignificant. A few studies even found antagonist effects and reduced toxicity associated with the combined exposure.

4.1. Bioaccumulation and effects in aquatic organisms

Co-exposure of aquatic organisms to MPs and emerging contaminants may affect different trophic levels. According to Table 2, most of the reviewed studies were performed on bivalves (n = 7), plankton (n = 6) and fish (n = 4) and mainly using PE (the most common MP polymers found in plastic debris), followed by PS. Laboratory experiments usually test non-contaminated organisms after ingestion of MPs or emerging pollutants alone and in combination of both types of pollutants. In addition to bioaccumulation, the study of different types of toxicity endpoints (oxidative stress, growth and survival, neurotoxicity and locomotor toxicity, gene expression, metabolic toxicity, inmunotoxicity, microbiome modulation or genotoxicity) on biota is generally included.Out of the 22 studies, 16 reported adverse effects caused by the co-exposure MP-emerging pollutants. Guilhermino et al. [68] reported that MPs and antibiotic florfenicol accumulate in the gut, gills, digestive gland, connective tissue, and hemolymphatic sinuses of *Corbicula uminea*. Overall, the concentration levels of florfenicol in animals exposed to MPs were higher than those found in animals exposed to florfenicol alone. Feeding inhibition, neurotoxicity and oxidative damage in *Corbicula uminea* was found to be higher after coexposure to MPs and florfenicol than single exposure. Triclosan accumulation in gills of *Perna canaliculus* was also found to be higher when adsorbed to PE, as well as the activity of antioxidative enzymes after combied exposure to triclosan and MPs [63]. Álvarez-Ruiz et al. [62] assessed the bioacummulation of 20 emerging pollutants in *Mytilus galloprovincialis* and showed that MPs acted as a vector for the bioaccumulation of PFASs, but not of chlorpyrifos, diclofenac and terbuthylazine. Furthermore, they also found that revomal of PFOS and perfluorodecanoic acid (PFDA) was slower in the mussels exposed to MPs. The ratio of elimination half-lives for the group exposed to emerging pollutants + MPs and the group exposed to mixture of emerging pollutants were > 1.63 and 2.69 for PFOS and PFDA, respectively. In another study, PS reduced the bioavailability and bioaccumulation of 6:2 chlorinated polyfluorinated ether sulfonate (F-53B) in zebrafish larvae but induced oxidative and inflammatory stress in zebrafish larvae [69]. In their experiments, authors observed a significant reduction in superoxide dismutase and lysozyme activity. The content of malondialdehyde and immunoglobulin M was not affected by F-53B or PS, but significantly increased in relatio to combined exposure. Furthermore, co-exposure significantly enhanced

protein expression of NF-*k*B and upregulated the expression of most immune-related genes. Rehse, Kloas and Zar [11] exposed freshwater zooplankton *Daphnia magna* to PA and BPA in different concentrations and found that exposure to PA particles alone did not lead to negative effects, while coexposure to BPA and MPs induced zooplankton immobilization. In studies with microalgae the effects on the growth or in the chlorophyll content are usually evaluated along exposure stage. Results from González-Pleiter et al. [24] concluded that exposure to MPs alone was not toxic to the cyanobacterium *Anabaena*, but exposure to MPs contaminated with antibiotics highly reduced the chlorophyll content and growth. Prata et al. [78]found that MP-procainaide and MP-doxycycline mixtures were more toxic than single exposure to each of the compounds to the marine microalgae *Tetraselmis chuii.*

Regarding higher organisms, Zhang et al. [10] suggested that coexposure to PS and roxithromycin might increase the bioaccumulation of this antibiotic in freshwater red tilapia (*Oreochromis niloticus*). The amount of PS in different tissues of tilapia was higher in the guts > gills > brain > liver; while for fish treated with roxithromycin and for the co-exposure group results were consistent and resulted in higher concentrations in the guts > liver > brain > gills. This accumulation pattern might be due to two uptake routes: gill adsorption and oral intake. Similarly, coexposure to PVC and venlafaxine resulted in higher concentrations of the antidepressant and its metabolites in loach liver tissue than exposure to venlafaxine alone [8]. Later, the same authors [9] demonstrated that co-exposure to methylamphetamine and MPs induces toxic effects and enantioselectivity of the CNS stimulant in aquatic species. Fonte et al. [71] reported that co-exposure to cefalexin and MPs significantly promoted toxicity in *Pomatoschistus microps* and the effect was more pronounced with increased temperature. Chen et al. [66] showed that BPA can accumulate in the viscera > gill > head > muscle of zebrafish and that co-exposure to BPA and NPs resulted in significantly higher bioaccumulation of BPA in the head and viscera. In addition, in the coexposure group the expression of most neurotoxic biomarkers is upregulated (*mbp* mRNA, *α1-tubulin* mRNA, dopamine and *manf* gene), suggesting an enhanced neurotoxic effect in both CNS and dopaminergic system. Conversely, the concentrations of BPA in muscle and gill of zebrafish did not significantly vary among exposure treatments. In a recent work, Beiras et al. [85] showed that the aquatic toxicity of MPs from conventional oil-based polymers is related to leaching of chemical additives, and not to direct interaction of plastic particles with marine organisms (microalgae (*Tisochrysis lutea* population growth), crustaceans (*Acartia clausi* larval survival), and echinoderms (*Paracentrotus lividus* sea-urchin embryo test)). The additives suspected to show toxicity were triclosan and, to a lesser extent, quercetin and lawsone. Replacement of synthetic triclosan by natural biocide lawsone slightly decreased the aquatic toxicity of the compounds.

On the other hand, of the 22 studies reviewed, only four have found antagonist effects related to co-exposure [70,74]. Brandts et al. [70] and Oliveira et al. [86] suggested that MPs might induce a potential protective effect against exposure to metals and some pharmaceuticals (antibiotics and carbamazepine). Brandts et al. [70] demonstrated that mussels are sensitive to PS. The abundance of mRNA revealed significant changes in the expression of genes associated with biotransformation and innate immunity in the gills or with DNA repair, and cell stress-response (especially in the digestive gland). Data from hemolymph showed decreased ChE activity, suggesting a possible neurotoxic action. However, the co-exposure to PS + carbamazepine reduced the toxicity of carbamazepine. In addition, coexposure resulted in specific responses (e.g. in gills downregulation in gene expression *hsp70*, *gst* and *p53* and *lys* mRNA or upregulation in gen *cyp11* mRNA) when compared to individual exposure, indicating activation of different response mechanisms. In line with this, Beiras et al. [64] concluded that exposure to PE in marine zooplankton did not enhance the toxicity of 4-n-Nonylphenol and 4-Methyl- benzylidene-camphor. Li et al. [77] studied the combined effect of dibutyl phthalate and PS on the marine copepod *Tigriopus japonicus* through both acute mortality tests and chronic reproduction tests. Antagonistic effects were observed for both tests. The LC_{50} of dibutyl phthalate was 1.23 mg/L, while exposure to PS did not have significant lethal effect on the copepods. The adsorption onto PS led to a decreased bioavailability of dibutyl phthalate. In contrast, chronic toxicity tests showed that exposure to lower concentrations of dibutyl phthalate did not affect the reproduction of the copepods, while PS reduced the number of copepod nauplii and extended the time to hatch. Similar results were reported by Zhang et al. [76]. PS, PS-COOH and PS-NH$_2$ reduced the toxicity induced by triphenyl phosphate in the larval locomotor activity (the movement duration and distance were increased 60–100%, in the coexposure groups). Moreover, the authors reported that the gene expression patterns induced in the group exposed to organophosphate flame retardant + MPs are indicative of different mechanisms involved in the reversal of the locomotor activity.

Overall, our results have revealed a lack of standardization in laboratory studies and in the testing conditions that reflect actual environmental exposure. The studies included in the present work investigate a wide range of concentrations of MPs (from 0.05 to 500 mg/L) and emerging pollutants (from 0.01 μg/L to 256 mg/L) as well as varying exposure times (from 1 day to 58 days). Most of the studies were conducted with commercial raw polymers, with little similarity in terms of shape and composition to environmental MPs. Experimental approaches using MPs of field origin are scarce [87]. Additional efforts are required to adapt the experimental conditions to provide robust and reliable data and deeply understand the relationship between ingestion rate and co-exposure effects. Further research is also needed to evaluate the effects of the weathering processes and particle size on MP ingestion. Furthermore, limited experimental information is available regarding other possible uptake routes in addition to ingestion. Jang et al. [88] compared particle ingestion and leachate uptake of the additive hexabromocyclododecane by exposing *Mytilus galloprovincialis* to two different sizes of PS (4.2–5.5 mm and 20–770 mm) and found that the uptake through the aqueous phase was more relevant than particle ingestion.

4.2. Bioaccumulation and effects in terrestrial organisms

One of the main routes for MPs to get into the soil is the application of treated sludge used as amendments to land. MPs are solid pollutants and as such they can led to changes in soil physical parameters (bulk density, water capacity…) and even the organic matter content [89]. de Souza Machado et al. [89] indicated that MPs might also change soil porosity, aggregation and water dynamics. Yan et al. [90] demonstrated that PP moves deeper into the soil with rain as a consequence of its hetero-aggregation and aging. Rillig et al. [91] also showed that MPs can increase water evaporation from soil through the formation of channels for water movements. This may result in drier soil conditions that might increase migration to deeper layers. The presence of high carbon polymers of MP could also cause the misjudgment of carbon storage in soil [92]. In this regard, Liu et al. [93] found that high concentrations of MPs in soil significantly increased the nutrients in DOM and nitrogen, phosphorus and carbon accumulation.

The presence of MPs in soil has also been found to influence the mobility of the sorbed pollutants [35,83]. Wang et al. [83] reported that the presence of PE in soil led to inhibition of ciprofloxacin degradation, and co-exposure significantly reduced soil microbial diversity. This is indicative that MPs can have an impact on terrestrial organisms, such as soil organisms, microbiota, and plants, involved in the functioning of terrestrial ecosystems. Chen et al. [35] investigated the adsorption-desorption behavior of triclosan to PE, PS, and soil particles and found that triclosan showed higher adsorption on MPs, particularly on PE, than on soil increasing the risk of triclosan mobility in soil. The equilibrium desorption of MPs was also higher than that of soil particles. The different behaviors of MPs and soil might lead to changes in the environmental behavior of triclosan in soil in the presence of MPs.

In contrast with the number of studies conducted on

Table 2
Details of co-exposure studies conducted with MPs and emerging compounds.

Media	Species	MP (type and concentration)	Emerging contaminant (type and concentration)	Type of experiment	Experiment	Effect type	Comments	Reference
Studies on aquatic organisms								
Aquarium (160 L)	Mussels (*Mytilus galloprovincialis*)	PE (1 mg per specimen)	4 pharmaceuticals, 4 pesticides and 4 PFASs (10 µg/L)	B	Exposure to ECs alone or in combination (ECs + PE). Exposure stage 0–28 days and depuration stage 29–58 days		PE favoured the bioaccumulation of PFASs and difficult their elimination from mussels. On the other hand, PE may reduce accumulation of pharmaceuticals and pesticides in mussel	[62]
Water	Green-lipped mussels (*Perna canaliculus*)	PE (0.5 g/L)	Triclosan (0.36 mg/L)	B+ T	Exposure to PE and triclosan alone or in combination for 48 h. Measurements of biomarkers	Synergistic	PE enhanced the uptake of triclosan in mussel. The co-exposure decreased oxygen uptake and byssus production. An enhanced effect was also observed on the SOD enzyme activity. These physiological responses were not observed when PE was spiked with triclosan	[63]
Water (50 mL)	Holoplanktonic copepod (*Acartia clausi*) and meroplanktonic larva (*Paracentrotus lividus*) sea-urchin	PE (1–10 mg/L)	Nonylphenol (4.1–77 µg/L) and 4-MBC (72–338 µg/L)	B +T	Exposure to PE and ECs alone or in combination for 96 h. Measurements of accute affects	–	Bioaccumulation was a linear function of waterborne chemical. MP never increased the bioaccumulation nor their toxicity to the exposed organisms disregarding the level of MP	[64]
Aquarium (500 L)	Whiteleg shrimp (*Litopenaeus vannamei*)	PS (0.69 mg/L)	BPA (2 µg/L)	B+ T	Control, exposed to PS, BPA and PS + BPA for 14 days. Measurement of gonadal development	Synergistic	MPs aggravated BPA accumulation in the gonad. The co-exposure increased the toxicity	[65]
Water (500 mL)	Adult zebrafish (*Danio rerio*)	PS NP (1 mg/L)	BPA (1 µg/L)	B + T	Exposure to PE and BPA alone or in combination for 3 days. Measurements of biomarkers	Synergistic	The co-exposure led to a significant increment of BPA uptake in the head and viscera. The co-exposure increased neurotoxic effects	[66]
Water (20 mL)	Freshwater microalgae (*Anabaena sp.* PCC7120)	PE, PA, PET, POM, PP, PS, PLA (150 beads/L)	Triclosan (0.7 mg/L)	B+T	Comparison of adsorption and desorption and effect on freshwater microalgae	Synergistic	PA>POM>LDPE retained sufficient amount of triclosan to desorbing it in concentrations high enough to induce toxic effects. Co-exposure led to a decrease in growth and chlorophyll a content	[67]
Water (170 mL)	Bivalves (*Corbicula fluminea*)	Red fluorescent polymer (0.2–0.7 mg/L)	Florfenicol (1.8–7.1 mg/L)	B + T	Exposure to MP and florfenicol alone or in combination for 96 h. Measurements of biomarkers	Synergistic	MPs were found in the gut, lumen of the digestive gland, connective tissue, hemolymphatic sinuses, and gills surface of animals. Florfenicol caused a significant inhibition of cholinesterase activity. MP caused a ChE activity inhibition. Mixture were more toxic	[68]
Aquarium (33.6 L)	Fish red tilapia (*Oreochromis niloticus*)	PS (100 µg/L)	Roxithromycin (50 µg/L)	B+T	Exposure to MP and roxythromycin alone or in combination for 14 days. Measurements of biomarkers	Antagonistic	PS enhance the bioaccumulation of roxithromycin in gut>gills>brain>liver. The neurotoxicity caused by ROX was alleviated	[10]

Table 2 (*continued*)

Media	Species	MP (type and concentration)	Emerging contaminant (type and concentration)	Type of experiment	Experiment	Effect type	Comments	Reference
							due to the presence of MPs. Oxidative damage in situations of co-exposure to MPs and ROX was mitigated	
Aquarium (30 L)	Loach (*Misgurnus anguillicaudatus*)	PVC (50–500 mg/L)	Venlafaxine and O-desmethylvenlafaxine (500 μg/ L)	S+B+T	Sorption and bioaccumulation experiments. Control, exposed to ECs and exposed to ECs + PVC. Exposure stage 16 days. Measurements of biomarkers	Synergistic	Co-exposure might lead to more adverse effects. Enantioselective behavior of venlafaxine and its metabolite occurred with R-enantiomers being preferentially degraded. BAF values were amplified more than 10 times with PVC in loach tissues	[8]
Water (glass beakers)	Zebrafish larvae	PS (50 μg/L)	6:2 chlorinated polyfluorinated ether sulfonate (F-53B) (10 μg/L)	B+T	Control, exposed to PS, F-53B and PS + F-53B for 14 days. Inmunotoxicity studies	Synergistic	PSs reduce the bioavailability and bioaccumulation of F-53B. Combined exposure of both pollutants induces oxidative stress and inflammatory response in zebrafish larvae	[69]
Aquarium (30 L)	Green algae (*C. pytenoidosa*) and freshwater snails (*C. cathayensis*)	PE (20 mg/L)	Methamphetamine (0.01–15 mg/L)	S+T	Sorption and bioaccumulation experiments. Control, exposed to ECs and methamphetamine alone and combined. Exposure stage 45 days. Measurements of accute afects	Synergistic	Acute toxicity of methamphetamine was significantly increased in the presence of PE. After ingestion, the enantioselectivity, BCFs, BMFs and distribution of methamphetamine were altered	[9]
Water (250 mL)	Freshwater zooplankton (*Daphnia magna*)	PA (200 mg/L)	BPA (10 mg/L)	T	Exposure to MP and BPA alone or in combination for 24–48 h. Measurements of acute effects	Antagonistic	The co-exposure decreased immobilization	[11]
Water (20 mL)	Freshwater microalgae (cyanobacterium *Anabaena sp.* PCC7120)	PET, PLA, POM, PE (1 g)	Azithromycin (500 μg/L) and clarithromycin (1000 μg/L)	T	Exposure to MP and antibiotics alone or in combination for 24–48 h. Measurements of acute effects	Synergistic	The co-exposure inhibited the growth and chlorophyll content	[24]
Water (1000 mL)	Mussel (*Mytilus galloprovincialis*)	PS (from 0.05 up to 50 mg/L)	Carbamazepine (6.3 μg/ L)	T	Exposure to MP and carbamazepine alone or in combination for 96 h. Measurements of biomarkers	Antagonistic	Combined exposure alleviate the toxicity of carbamazepine and induce specific responses when compared to individual exposure (e.g. in gills downregulation in gene expression *hsp70, gst* and *p53* and *lys* mRNA or upregulation in gen *cyp11* mRNA)	[70]
Water (500 mL)	Common goby (Pomatoschistus microps)	PE (0.184 mg/ L)	Cefalexin (1.3–10 mg/ L)	T	Control, exposed to cefalexin and PE alone and combined. Exposure stage 96 h. Measurements of accute afects	Synergistic	The rise of water temperature increased the MPs-induced mortality and the inhibitory effects of cefalexin on the PEPP	[71]
Aquarium (350 L)	Oyster (*Crassostrea brasiliana*)	PE (22.5 g)	Triclosan (1 mg/L)	T	Control, exposed to EC and exposed to EC + PE for 3 or 7 days. Measurements of biomarkers	Synergistic	Ability of PE to carry triclosan to oyster and physiological disturbances	[72]
Aquarium (40 L)	Clams (*Tegillarca granosa*)	PS different sizes (diameter	Sestraline (0.1 μg/L)	T	Control, exposed to PS, Sertraline and PS	Synergistic	The co-exposure suppressed the immune	[73]

Table 2 (*continued*)

Media	Species	MP (type and concentration)	Emerging contaminant (type and concentration)	Type of experiment	Experiment	Effect type	Comments	Reference
		500 nm and 30 μm) (0.29 mg/L)			+ Sertraline for 14 days. Inmunotoxicity studies		responses. The toxic effect of Setraline was not affected by microscale MPs while an evident synergistic immuno-toxic effect was observed with NPs	
Aquarium (30 L)	Clams (*Tegillarca granosa*)	PS (1 mg/L)	BPA (0.01 and 0.1 0.1 μg/L)	T	Control, exposed to PS, BPA and PS + BPA for 14 days. Inmunotoxicity studies	Synergistic	The co-exposure led to an increase of neurotransmitters but a decrease in the expression of genes encoding modulatory enzymes and receptors for these neurotransmitters	[74]
Water (glass beakers)	Zebrafish larvae	PS (2 mg/L)	Butylated hydroxyanisole (1 mg/L)	T	Control, exposed to PS, CE and PS + CE for 7 days. Toxicity studies	Synergistic	MPs promoted the accumulation of butylated hydroxyanisole in zebrafish larvae and enhanced the toxicity in larvae development manifested by reduced hatching rates, increased malformation rates and decreased calcified vertebrae.	[75]
Water (glass beakers)	Marine medaka (*Oryzias melastigma*) larvae	PS, PS-COOH and PS-NH2 (20 μg/L)	Triphenyl phosphate (20 and 100 μg/L)	T	Control, exposed to MPs, EC and MPs + CE for 7 days. Toxicity studies	Antagonistic	PS, PS-COOH and PS-NH2 alleviate the toxicity induced by triphenyl phosphate in the larval locomotor activity (the movement duration and distance moved were increased 60–100%, in the coexposure groups)	[76]
Water (glass beakers)	Copepod (*Tigriopus japonicus*)	PS (20–500 mg/L)	Dibutyl phthalate (0.125–8 mg/L)	T	Control, exposed to PS, EC and PS+ CE for 96 h. Toxicity studies	Antagonistic	The LC50 of dibutyl phthalate was 1.23 mg/L, while exposure to PS didn't have significant lethal effect on the copepods. The adsorption onto PS led to a decreased of the bioavailability of dibutyl phthalate, resulting in decreased toxicity.	[77]
Culture medium (glass beakers)	Microalgae (*Tetraselmis chuii*)	Red fluorescent polymer microspheres (1.5 mg/L)	Procainamide, doxycycline (4–256 mg/L)	T	Single and combined effects of MP and pharmaceuticals at different concentration levels	Synergistic	MP-procainamide and MP-doxycycline mixtures were more toxic than alone	[78]
Studies on terrestrial organisms								
Sludge (450 mL serum +100 mL)	Hydrogen-producing thermophilic bacteria	PS (0.2 mg/L)	PFOS (0.1–5 mg/L)	T	Single and combined effects of PS and PFOS on hydrogen-producing thermophilic bacteria (7 days at 55 C and pH = 5.7)	Antagonistic	The combined pollutants lead to a 31.6% reduction in hydrogen production. The addition of PFOS alleviated the toxic effect of PS, but did not change its mechanism of toxicity	[79]
Soil	Soil organisms (*Caenorhabditis elegans* and *Zea mays*)	PE (0.1% w/w)	Pharmaceuticals (3) and pesticide (1) (15 μM)	T	Soil contaminated with ECs and PE (alone or in combination) for 30 days	–	MP or mixture treatments negatively impacted Zea mays and the soil bacterial community. Soil treated with MPs or mixture did not affect the nematode Caenorhabditis elegans.	[80]
Soil	Earthworms (*Eisenia fetida*)		PFOA and PFOS (5–10 mg/kg)	B + T	Soil contaminated with PFASs and PVC	Synergistic	The presence of PVC increased the	[81]

Table 2 (*continued*)

Media	Species	MP (type and concentration)	Emerging contaminant (type and concentration)	Type of experiment	Experiment	Effect type	Comments	Reference
		PVC (0.1–1000 mg/kg)			(alone or in combination) for 14 days		bioaccumulation of PFASs up to 200% in earthworms. Significant reduction in their reproduction was observed	
Soil	*Enchytraeus crypticus* microbiome	PA and PVC (1000 mg/kg)	Tetracycline (20 mg/kg) and ARGs	B	Exposure to MP and tetracycline alone or in combination for 48 h. Measurements of biomarkers	–	MPs and tetracycline significantly disturbed the microbial community, and decreased the microbial alpha diversity. There were no significant differences between alone and combination exposure	[82]
Soil	Microbial communities	PE (1% w/w)	Ciprofloxacin (10 mg/L)	D	Degradation studies of ciprofloxacin in soil and soil amended with MP.	–	Co-exposaure decreased the microbial diversity. Serratia and Achromobacter were abundant in the MPs-ciprofloxacin co-amended soil	[83]
Soil	–	40 mg MP (PE, PS) and 40 mg soil	Triclosan (1.8–11 mg/L)	S	Comparison of adsorption and desorption of triclosan in soil and MPs	–	PS and soil had similar adsorption kinetic process, while PE exhibited higher adsorption rate and equilibrium capacity than soil	[35]
Soil	–	PVC, PE, PS (1000 mg/kg)	17β-estradiol (E2) (0.25–10 mg/L)	S	Sorption experiments: Comparison soil and MP	–	The adsorption capacity of MPs to E2 is stronger than that of soil. MPs reduce the mobility of E2 by improving the adsorption capacity of the soil	[84]

Type of experiment: B: Bioaccumulation studies; T: Toxicity studies;; S: Sorption studies; D: Degradation studies; EC: Emerging contaminant; PE: polyethylene; PA: polyamide; PET: Polyethylene terephthalate; POM: polyoxymethylene; PP: polypropylene; PS: polystyrene; PLA: polylactic acid.

bioaccumulation and toxicological effects of co-exposure to MPs and emerging pollutants in marine organisms, little research has been done on terrestrial organisms (Table 2). One of these few studies is the one by Sobhani et al. [81] who estimated an increase of the bioaccumulation factor of PFOA and PFOS above 200% in earthworms exposed to PVC-contaminated soil. Co-exposure to MP-PFASs increased the uptake of PFOS and PFOA in earthworms and a significant decline in their reproduction. Recently, Martín et al. [94] evaluated the effects of exposure to PE, simazine and ibuprofen on *Caenorhabditis elegans* and *Lactuca sativa* and reported harmful effects on *C. elegans* in relation to single exposure to PE but more harmful effects were seen after co-exposure to PE and emerging pollutants. Co-exposure to PE and simazine led to inhibition of leaf growth and seed germination in *Lactuca sativa*. Fajardo et al. [80] found different interaction behaviour depending on the type of PE and pollutant. White PE selectively adsorbed higher amounts of sulfadiazine, but blue and fluorescent blue PE preferably adsorbed amoxicillin. The presence of MPs and pharmaceuticals in soil did not seem to affect the nematode *Caenorhabditis elegans* but it negatively affected Zea mays and the soil microbial community, which can be explained by the complex complex structure and the multiple interactions that occur in soil. Dólar et al. [95] provided evidence that the changes in the immune system induced by exposure to mixtures of chlorpyrifos and MPs in terrestrial *Porcellio scaber* differ from those induced by individual exposures. Alterations in some measured parameters (acetylcholinesterase activity and haemocyte viability) suggested a reduced bioavailability of chlorpyrifos caused by MPs exposure, but the increase of haemocyte count was promoted by the

presence of polyester fibres denoting their joint action. Co-exposure to MPs and antibiotics might also increase the development of antibiotic resistance genes (ARGs) [82,96,97]. Co-exposure to MPs and tetracycline led to significant disruption of the microbial community in *Enchytraeus crypticus* microbiome [82]. It was also found that exposure to PA, PVC and tetracycline results in higher abundance of ARGs in *E. crypticus* compared to single exposure to MPs: However, no differences in tetracycline accumulation were found between exposure to tetracycline alone, PA and tetracycline, and PVC and tetracycline in *E. crypticus*. Lu et al. [97] found a higher abundance of ARGs on MPs in agricultural soil when MP particles were larger and highly weathered or from soil with long cultivation periods. Selective enrichment of ARGs also depends on the specific ARG type. In this regard, the genes conferring resistance to macrolide, lincosamide, and streptogramin B antibiotics and sulfonamide were found to be selectively enriched on highly weathered MPs, while genes conferring resistance to aminoglycosides and beta-lactamases were enriched on slightly weathered MPs. However, research on the mechanisms associated to increased toxicity in relation to co-exposure to MPs and other contaminants is scarce and further studies are needed.

5. Bioaccesibility/bioavailability of microplastics-associated emerging pollutants

Anorther point to consider is that, after ingestion of contaminated MPs by organisms, the digestive fluids promote pollutant desorption. This could be explained by the effect of gastrointestinal fluids in the

protonation and deprotonation at different pH, which have an impact on their solubility and, in turn, in their desorption capacity [7,60,61]. The presence of gastrointestinal fluids, whose secretion is induced at low pH, results in 30-fold higher desorption of DDT, phenanthrene, PFOA and di-2-ethylhexyl phthalate from PVC and PE than in seawater [60]. Wu et al. [98] concluded that gastric fluids enhance hormone desorption from PVC as consequence of the low pH and increase in ionic strength. Moreover, the studies showed that desorption of tetracycline, amlodipine, and atorvastatin increases in gastrointestinal conditions in relation to high temperatures, which means warm-blooded organisms are at higher risk than cold-blooded organisms [7].

MP aging induced bioaccessibility changes, which confirms the important roles of MP structures and surface polarity in sorption and desorption hysteresis and, consequently, in the gastrointestinal bioaccessibility. Liu et al. [7] examined the effect of MP aging on the desorption of atorvastatin and amlodipine in artificial gastric and intestinal fluid and seawater and found that intestinal fluid increased atorvastatin desorption and gastric fluid increased amlodipine desorption. MP aging suppressed overall desorption in relation to decreased hydrophobicity caused by the presence of oxygen-containing groups on the surface. In contrast, for tetracycline and ciprofloxacin antibiotics the desorption rates decreased with MP aging as the binding strength was increased, but on the other way the desorption capacities increased in artificial intestinal fluid [22]. In another attempt, using an in-vitro digestive model Liu et al. [99] showed that the gastrointestinal bioaccessibility of MP-associated pyrene and 4-nonylphenol can be high and in wide ranges: $16.1 - 77.4\%$ and $26.4 - 83.8\%$, respectively. The structural rigidity of MPs was an important factor controlling bioaccessibility of pyrene (a nonpolar a nonionic molecule), likely by inducing its physical entrapment in porous domains, whereas polarity of MPs controlled bioaccessibility of 4-nonylphenol, by regulating polar interactions. Assuming an ingestion rate of 950 particles/day, a concentration of pollutants associated to MPs of 400 mg/kg for pyrene and 4000 mg/kg for 4-nonylphenol and using the bioaccessibility observed in this study, the calculated daily intake values are 3.28×10^{-4} to 1.58×10^{-3} mg/kg/day for pyrene and 1.51×10^{-2} to 4.78×10^{-2} mg/kg/ day for 4-nonylphenol. Nevertheless, these pollutant concentrations are relatively high and the actual bioaccessibility may be lower.

Recently, López-Vazquez et al. [100] investigated humand ingestion of plastic additives and monomers using bioaccessibility tests under fed and fasting conditions and found that oral bioaccessibility accounts for more than 65% of overall bioaccessibility and increases significantly for dimethyl phthalate, diethyl phthalate and BPA. Significantly greater bioaccessibility was found for LDPE against PVC, which was attributed to their differential chemical sorptive properties. The structural rigidity of the glassy PVC might lead to significant irreversible desorption and low diffusion kinetics of the most hydrophobic compounds from the rigid pores, and the increased surface polarity of PVC that fosters adherence of the most polar additives. The estimated human average daily intake, using the overall oral bioaccessibility data measured, indicated that MPs containing dimethyl phthalate, di-n-butyl phthalate and BPA at $> 0.3\%$ (w/w) might pose risks to human health.

6. Conclusions

The interactions between MPs and emerging contaminants are becoming issues of concern. Available research on the sorption process has been done primarily on PE followed by PS, PVC, PA and PP. Adsorption on MPs is mainly driven by hydrophobic and electrostatic interactions. However, due to specific polymer–pollutant interactions as well as the effect of weathering and environmental factors, the sorption mechanisms cannot be completely predicted. Porous filling, hydrogen and π-π bond interactions also participate in adsorption. Sorption experiments have revealed that PA has the highest adsorption capacity to more polar emerging pollutants like antibiotics and BPA, which can be attributed to the presence of complex hydrogen bonds and its porous

structure. In addition, MP aging increases the surface hydrophilicity, which leads to increased toxicity and adsorption of these pollutants.

Despite the abundance of recent studies on sorption process, there is a lack of field experiments outside of laboratory settings. Conclusions on sorption mechanims have been drawn from laboratory batch studies usually using commercial raw polymers and single solute system. Due to the significative effect of aging, MP type, particle size, pH, ionic strength, and DOM in the matrix, which either promote or suppress sorption, it seems appropriate to conduct laboratory experiments and parallel field experiments. In addition, unlike pharmaceuticals as antibiotics, and some particular personal care and household products (as the antimicrobial triclosan or some PFASs) which have been relatively well-investigated, other therapeutic groups such as antidepressants, β-blockers, NSAIDs, and steroid hormones as well as household (surfactants) or personal care products (preservatives and ultraviolet filters) should be included in further studies.

Co-exposure studies in biota have yielded different results, sometimes even contradictory. A high number of studies found adverse effects related to co-exposure to MPs and emerging pollutants, while other studies found that these effects were practically insignificant. A few studies even found antagonist effects and reduced toxicity associated with co-exposure. The studies reviewed used different experimental designs, exposure time, MP sizes and polymer types and different pollutants. Extensive research is still needed to achieve a complete understanding of the effects of the exposure to MPs, alone or in combination with other pollutants. In addition to PS and PE, future studies should include a larger number of MPs and actual environmental concentrations, as they are usually higher. There is also a clear lack of data on the interactions in terrestrial organisms.

Finally, standardised sampling procedures and analytical methods for the extraction and determination of emerging pollutants adsorbed onto MPs are urgent in order to determine the extent of this problem and to fully understand its effects on living organisms.

Declaration of Competing Interest

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

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