



Evaluation of European watch list contaminants in environmental matrices and microplastics: Analytical strategies, mechanisms of adsorption and occurrence

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ABSTRACT

The European Union requires environmental monitoring to identify potential pollutants suspected of causing adverse effects, affecting not only aquatic organisms but also posing direct and negatively influence to human health. Comprehensive knowledge about their occurrence and impact of these pollutants in environmental matrices, including microplastics, is essential for informed decision regarding their inclusion in surveillance lists. This study focuses on reviewing and assessing the analytical methodologies employed in determine substances listed in the last 4th European Watch List, in various environmental matrices, including water, soils, biota, and microplastics. Additionally, the different interaction mechanisms of adsorption onto microplastics are discussed. A dedicated section is also addressed to examine the occurrence of these substances in diverse environmental matrices. The findings contribute to a better understanding of the presence and effects of these substances, aiding in the development of effective surveillance strategies to mitigate their impact on the environment.

1. Introduction

Despite the obvious effort to improve the quality of the environment, the trend of environmental pollution by human activity with substances harmful to the environment as well as to humans continues. It is

therefore important to determine which substances belong or may belong to this category.

The Commission Implementing Decision of European Union (EU) at first established defined 1st Watch List (WL) for substances in surface waters (2015/495) under the Environmental Quality Standards

Abbreviations: AA-IL-DLLME-SA, Air-assisted ionic liquid dispersive liquid–liquid microextraction based on solidification of aqueous phase; AALLME, Air assisted liquid microextraction; CB, Chlorobenzene; DAD, Diode array detection; DDT, Dichloro-diphenyl-trichloroethane; DLLME, Dispersive liquid liquid microextraction; DOM, Dissolved organic matter; D_{ow} , Octanol-water distribution ratio; DSPE, Dispersive solid phase extraction; EC, European Commission; EQSD, Environmental Quality Standards Directive; EU, European Union; FLD, Fluorescence detection; FPSE, Fabric phase sorbent extraction; GC, Gas chromatography; GO-d-SPE, Graphene oxide GO based dispersive-solid phase extraction; HF-SPME, Hollow fiber solid phase microextraction; HPLC, High performance liquid chromatography; HRMS, High resolution mass spectrometry; K_D , Distribution coefficient; K_f , Adsorption coefficient; K_{ow} , Partition coefficient; LC, Liquid chromatography; LOD, Limit of detection; LOQ, Limit of quantification; LTPE, Low temperature partitioning extraction; MASPE, Microwave assisted solid phase extraction; MDL, Method detection limit; ME, Matrix effect; META-IL-DLLME, Magnetic effervescent tablet assisted ionic liquid dispersive liquid liquid microextraction; MIP-SPE, Molecularly imprinted polymer solid phase extraction; MP, Microplastic; MQL, Method quantification limit; MS, Mass spectrometry; MS/MS, Tandem mass spectrometry; MSPE, Magnetic solid phase extraction; OP, Organic pollutants; PA, Polyamide; PAH, Polycyclic aromatic hydrocarbons; PBS, Polybutylene succinate; PCB, Polychlorinated biphenyls; PE, Polyethylene; PET, Polyethylene terephthalate; PHWE, Pressurized hot water extraction; P_{Ka} , Acid dissociation constant; PLA, Polylactic acid; PNEC, Predicted no effect concentration; POCIS, Polar Organic Chemical Integrative Samplers; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl chloride; PZC, Point of zero charge; QTOF, Quadrupole time of flight; QuEChERS, Quick Easy Cheap Effective Rugged Safe; SALLME, Salt assisted liquid liquid microextraction; SLE, Solid liquid extraction; SPE, Solid phase extraction; SPME, Solid phase micro extraction; SS-LPE, Switchable solvent liquid phase extraction; TC, Tetracycline; UAE, Ultrasound assisted extraction; UPLC, Ultra performance liquid chromatography; USAEME, Ultrasound-assisted emulsification microextraction; UV, Ultraviolet; VASE, Vacuum assisted sorbent extraction; VIS, Visible light; WL, Watch list.

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Directive (EQSD - Directive 2008/105/EC) in March 2015 [1] and contained 10 individual or groups of substances. The primary purpose of the EU watch list is to identify emerging pollutants occurring in various countries within the EU and to implement regulatory measures through technical monitoring approaches of their occurrence and prevalence. Emerging pollutants listed on the watch list are assessed for their potential risks and managed accordingly. The process for selecting candidate substances for the WL is comprehensive, and includes several factors such as hazard properties, ecotoxicology, and monitoring data. Substances on the WL are chosen because they may pose a significant risk to or through the aquatic environment, although they have not yet been demonstrated to pose a real risk due to insufficient monitoring data. Despite this, these substances are not regularly monitored even though they are discharged into the aquatic environment [2].

The WL of substances has been updated several times since its inception. Some substances that were included in the early versions, such as diclofenac (an anti-inflammatory drug), and the hormones 17-beta-estradiol (E2) and 17-alpha-ethinylestradiol (EE2), were later removed. These removals can occur for various reasons, such as the availability of better monitoring data indicating a lower risk or the implementation of regulatory measures that mitigate the associated risks. Similarly, updates to the WL have also involved the addition of new toxic substances, such as metformin, amoxicillin and ciprofloxacin in 2018 and sulfamethoxazole and trimethoprim, venlafaxine, o-desmethylvenlafaxine, dimoxystrobin and famoxadone in 2020. At the same time, according to Article 8b of the EQSD, the continuous monitoring period for any WL substance should not exceed four years. The last update the 4th WL of substances for Union-wide monitoring in the field of water policy pursuant was established by the European Commission (EC) on July 22, 2022 [3]. Finally, two antibiotics (clindamycin and ofloxacin), three pesticides (azoxystrobin, diflufenican and fipronil), group of sunscreen agents (avobenzone, octocrylene and oxybenzone) and the pharmaceutical substance for type 2 diabetes treatment (metformin) and its transformation product guanylurea were added to the WL. For both the antibiotics clindamycin and ofloxacin as antibacterial agents, their widespread use in veterinary and human medicine has been found to cause increased releases to waterways, which may contribute to the spread of antimicrobial resistance (AMR) to aquatic organisms. All mentioned three pesticides are persistent and toxic to aquatic environment or organisms. Fungicide azoxystrobin and herbicide diflufenican are approved for use as plant protection products (PPP) and insecticide fipronil is an approved for use as a biocide in the European Environment Agency (EEA) and/or Switzerland. Avobenzone, octocrylene and oxybenzone are used as UV filters in personal care, cosmetics, and industrial products. They are bioaccumulative, persistent and toxic, so their direct washing into any waters can be a major problem. However, no experimental data on the standard long-term toxicity of these substances are currently available. Since avobenzone and octocrylene are highly hydrophobic, the recommended matrices for their monitoring are sediment and biota as opposed to the less hydrophobic oxybenzone where it is water or sediment. Metformin is a human drug used to treat type 2 diabetes and, along with the degradation product guanylurea, has been determined in water to have demonstrable estrogenic effects. The final composition of the 4th WL substances and some of their properties are given in Table 1 [3]. In addition, it is crucial to consider the toxicity of the watch list (WL) compounds. Many of these substances, while not extensively studied in all contexts, have been identified as hazardous due to their potential adverse effects on human health and the environment. For instance, compounds such as benzophenone-3, dimoxystrobin, famoxadone, fluconazole, imazalil, metconazole, ofloxacin, penconazole, sulfamethoxazole, tebuconazole, trimethoprim or venlafaxine and its metabolite, have been linked to various toxicological concerns including carcinogenicity, endocrine disruption, and neurotoxicity. Understanding the toxic effects of these compounds is essential for developing effective regulatory measures and mitigating their impact.

The presence of these pollutant compounds in the environment is more concerning considering that they do not appear individually, but as a complex mixture, which could lead to unwanted synergistic effects. From the point of view of monitoring the 4th WL substances it is essential to conduct a detailed analysis across various environmental matrices highlight their widespread distribution. This analysis should extend not only in surface water [4] but also in other environmental samples such as drinking water [5], wastewater [6], seawater [7], soil [8], sediments [9] or biota [10].

The growing concern about the presence of these compounds in the environment is clearly reflected in the significant increase in research paper on this topic over the last 20 years. Fig. 1 shows the time evolution of the number of papers published on this topic in the Scopus database using the keywords such as watch list (OR) determination (OR) analysis (OR) occurrence from 2000 to 2023. The number of articles has increased from just over 200 in the year 2000 to more than 900 in 2023. This not only highlights an increased awareness of potential environmental impacts but also underlines the need to better understanding of the associated risks and find sustainable solutions.

Moreover, an additional concern is related with the presence of microplastics (MPs) in the environment. Their occurrence has been reported in worldwide showing a widespread distribution, from remote areas to densely populated regions and throughout the marine environment. The MPs have been considered pollutants in themselves, about the possible negative impact on the health of marine organisms [11]. However, it is also necessary to consider their behaviour as matrices, due to their ability to adsorb organic and inorganic pollutants on their surface and act as a transmission vehicle for these contaminants to the organisms [12]. MPs can increase the bioavailability of these pollutants in the organisms through of their Ingestion and then increase the dose of contaminants to consumers. Several authors and research teams have investigated the organic substances adsorbed onto MPs. However, published studies often focus on specific groups of substances, such as persistent organic pollutants, UV filters, and hormones. In addition, other watch list compounds, such as miconazole and trimethoprim, have also been studied.

Therefore, it is important developed analytical strategies that allow the determination and presence of contaminants of interest from the 4th WL substances in different environmental compartments, and those adsorbed on the surface of MPs.

An important evaluation criterion for these analytical methods is their sensitivity, preferably expressed as a limit of quantification (LOQ) or limit of detection (LOD) value depending on the type of matrix [2]. Therefore, the combining extraction/preconcentration, highly performance separation and sensitive detection methods are predominantly used for this purpose.

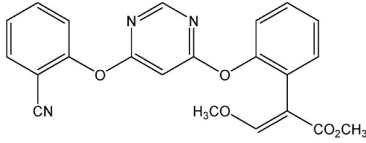
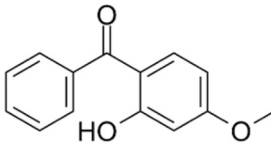
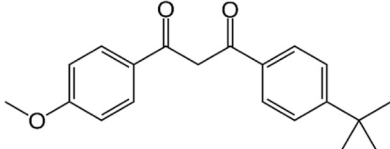
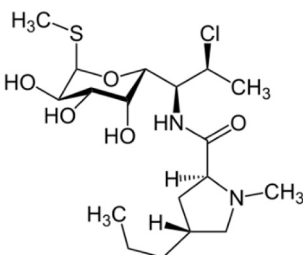
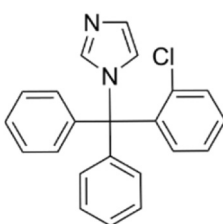
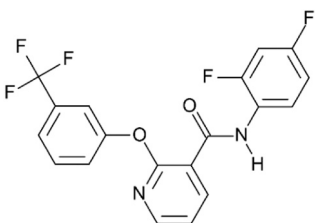
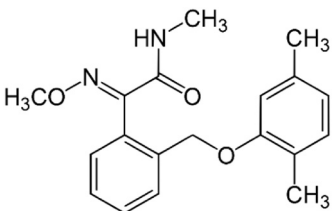
In this review, it is offered to readers an overview of articles dedicated to the determination and occurrence of 4th WL substances in various environmental samples including water, soils, biota and microplastics. Based on this revision, Fig. 2 illustrates the distribution of contaminants from the 4th WL in different environmental matrices, with approximately 68 % of the findings reported in liquid samples and 65 % in solid samples, and 8 % in microplastics.

Firstly, the analytical methodologies used in this topic are critically discussed and evaluated their advantages and disadvantages associated with their sensitivity and the influence of different types of matrices on the analysis. In the following, the interactions of 4th WL substances with microplastics, such as their sorption mechanism, sorption kinetics, and isotherms are described in detail. In a separate section, occurrence of 4th WL substances in different environmental matrices is also overviewed. The content of this work may constitute an important contribution in the field of environmental impact of the substances studied.

2. Analytical methods

The analysis of contaminants in environmental samples typically

Table 1
Some characteristics of substances from the 4th European Watch List.

Substance	Mr [g mol ⁻¹]	log K _{ow}	Use	Hazard properties	Structure
Azoxystrobin	403.39	2.5	It is approved as a fungicide in PPP and is also used for preserving construction materials	It is very toxic to aquatic life and aquatic life with long lasting effects	
Benzophenone-3 (Oxybenzone)	228.24	3.79	Used in cosmetics as UV-filter in sunscreen products and coating products, fillers, putties, plasters, modelling clay and finger paints	It is very toxic to aquatic life and aquatic life with long lasting effects, under assessment as endocrine disrupting	
Butyl methoxydibenzoylmethane (Avobenzone)	310.4	4.51	It is a full-spectrum UVA blocker, widely used in cosmetic products worldwide	Suggested that functions as a metabolic disrupting obesogen, under assessment as persistent, bioaccumulative and toxic	
Clindamycin	424.98	2.16	Pharmaceutical use as antibiotic (lincosamide)	It is suspected to be toxic to reproduction	
Clotrimazole	344.84	6.26	Pharmaceutical use as an antifungal medicine to treat skin infections caused by a fungus	Causes harm if ingested, results in serious eye irritation, skin irritation, and is highly toxic to aquatic life	
Diflufenican	394.29	4.90	It is herbicide used as PPP	It is very toxic to aquatic life and aquatic life with long lasting effects	
Dimoxystrobin	326.4	3.59	It is mainly used as a fungicide used for disease control in cereals and some other crops	Persistent, highly toxic, suspected of causing cancer and damaging fertility or the unborn child, and is also an endocrine disruptor	

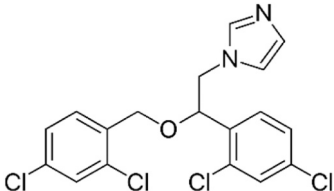
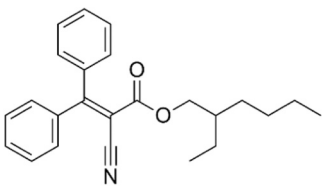
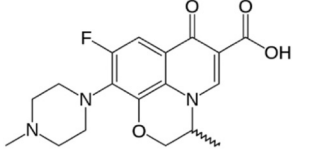
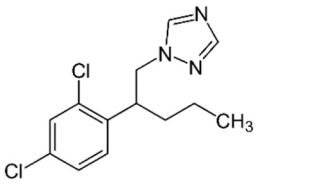
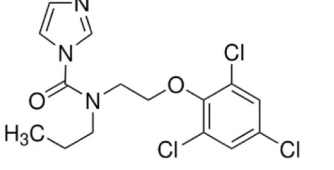
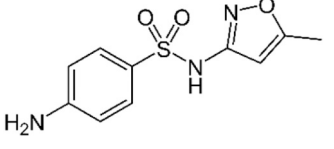
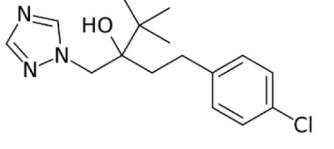
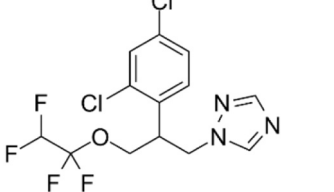
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Table 1 (continued)

Substance	Mr [g mol ⁻¹]	log K _{ow}	Use	Hazard properties	Structure
Famoxadone	374.4	4.65	It is a fungicide for the control of various fungal diseases on plants (oxazolidinedione)	It is a neurotoxicant and is a known eye and skin irritant, also is highly toxic to aquatic and terrestrial organisms	
Fipronil	437.15	4.0	Veterinary use as an insecticide	It is very toxic to aquatic life with long lasting effects	
Fluconazole	306.27	0.25	Pharmaceutical use as an antifungal medicine to treat infections caused by different kinds of fungus	It poses a risk if ingested, may harm the unborn child, and is highly detrimental to aquatic organisms, resulting in long-term adverse effects	
Imazalil (Enilconazole)	297.18	3.82	It is a systemic fungicide inhibiting the biosynthesis of ergosterol and effectively combats a broad spectrum of fungal diseases in fruits, vegetables, and ornamental plants	It causes serious eye irritation, is harmful if inhaled, suspected of causing cancer and very toxic to aquatic life with long lasting effects	
Ipconazole	333.86	4.3	It is triazole fungicide used to control a range of soil and seed borne seed diseases in a wide range of crops	It is classified as very persistent and toxic to terrestrial organisms and aquatic life with acute and long lasting effects	
Metconazole	319.83	3.85	It is triazole fungicide used to control a range of fungal infections on fruit and other crops	It is harmful if swallowed or inhaled, suspected of damaging fertility or the unborn child, and toxic to aquatic life with long lasting effects	
Metformin and its transformation product Guanylurea	129.16 102.10	-2.64	Pharmaceutical use as an antidiabetic for the treatment of type 2 diabetes	It is harmful if swallowed, causes skin and serious eye irritation	Metformin
					Guanylurea

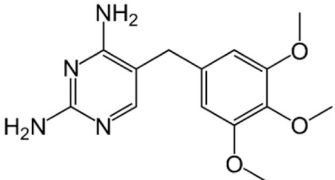
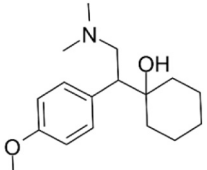
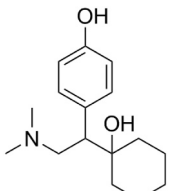
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Table 1 (continued)

Substance	Mr [g mol ⁻¹]	log K _{ow}	Use	Hazard properties	Structure
Miconazole	416.13	6.1	Pharmaceutical use as an antifungal medication used to treat fungal skin infections	It is harmful if swallowed, very toxic to aquatic life and aquatic life with long lasting effects	
Octocrylene	361.48	6.88	Industrial and cosmetic use as UV-filter	It is currently under ECHA's evaluation as a potential PBT substance and is considered as a suspected endocrine disruptor	
Ofloxacin	361.37	-0.39	Pharmaceutical use as an antibiotic to treat bacterial infections in the body (fluoroquinolone)	It is harmful if swallowed or in contact with skin, may cause allergy or asthma symptoms, suspected of causing genetic defects and fertility or the unborn child	
Penconazole	284.2	3.72	It is a triazole fungicide used to control powdery mildew by inhibiting sterol biosynthesis in fungi	It is suspected of damaging fertility or the unborn child, toxic if inhaled and swallowed, and very toxic to aquatic life with long lasting effects	
Prochloraz	376.7	3.53	It is an imidazole fungicide widely used in gardening and agriculture	It is harmful by inhalation, in contact with skin and if swallowed, also very toxic to aquatic life with long lasting effects	
Sulfamethoxazole	253.28	0.89	It is a sulfonamide antibiotic that aids in the treatment of various bacterial infections	It may cause genetic defects, is suspected of causing cancer and very toxic to aquatic life with long lasting effects	
Tebuconazole	307.82	3.7	It is a triazole fungicide that stops the growth of fungi by blocking the synthesis of sterols in plants	It is harmful if swallowed, suspected of causing harm to fertility or the unborn child, toxic to reproduction, and highly toxic to aquatic life with long lasting effects	
Tetraconazole	532.46	3.56	It is a chiral triazole fungicide widely used for preventing plant diseases in wheat fields	It is harmful if swallowed or inhaled, toxic to aquatic life with long lasting effects	

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Table 1 (continued)

Substance	Mr [g mol ⁻¹]	log K _{ow}	Use	Hazard properties	Structure
Trimethoprim	290.32	0.91	It is an antibiotic used to treat bladder or kidney infections, or ear infections caused by certain bacteria	It is harmful if swallowed or inhaled, suspected of damaging the unborn child and toxic to aquatic life with long lasting effects	
Venlafaxine and its metabolite O-desmethylvenlafaxine	277.40 263.37	3.20 0.21	It is a serotonin-norepinephrine reuptake inhibitors used as antidepressant to treat depression, anxiety or panic attacks	It is harmful if swallowed, causes serious eye irritation, may damage fertility, the unborn child or breast-fed children and is toxic to aquatic life with long lasting effects	 

* PPP – Plant protection product; PBT – Persistent, bioaccumulative and toxic; ECHA – European Chemicals Agency

Documents by year

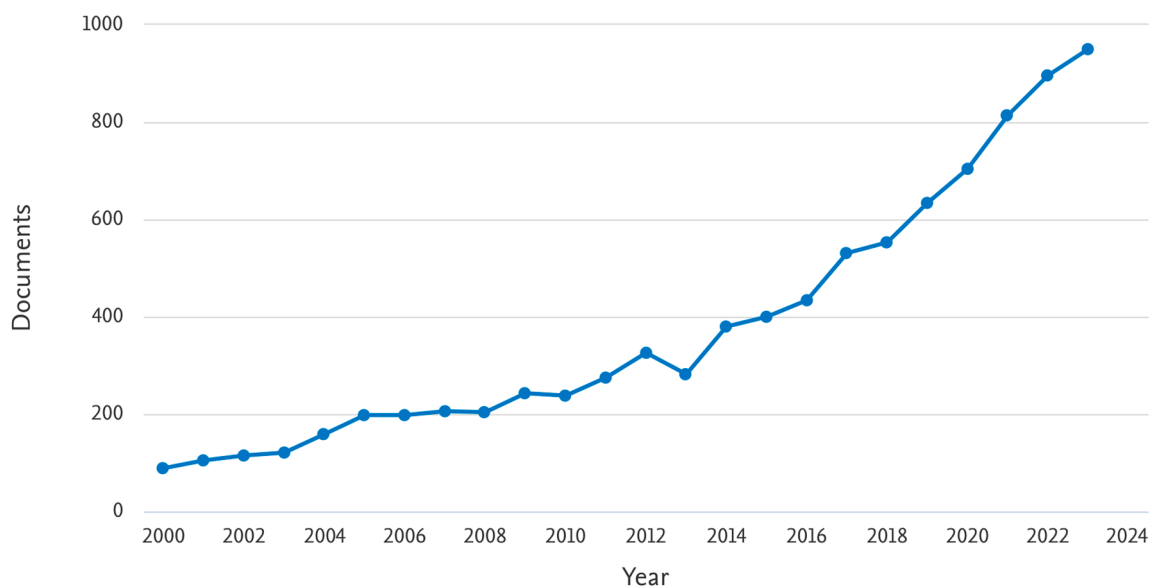


Fig. 1. Evolution of the number of publications devoted to a given topic from the Scopus database from 2000 to 2023 (searched keywords: watch list, determination, analysis, occurrence; accessed in December 2023).

demands intricate sample processing owing to the low concentrations at which these contaminants are present. Extracting various contaminants poses a significant challenge for scientists prior to their determination process. Consequently, despite the frequent utilization of highly sensitive and selective analytical techniques like chromatographic methods coupled with tandem mass spectrometry (MS/MS) or high-resolution mass spectrometry (HRMS), obtaining clean extracts is critical to mitigate potential instrumental issues or quantification errors. These errors

may stem from factors such as the matrix effect (ME) or interference from other compounds.

The contaminants present in the 4th WL have different physical-chemical properties, with polarities ranging from 0.21 (O-desmethylvenlafaxine) to 6.88 (Octocrylene) (Table 1), and therefore it is necessary to select the appropriate extraction and determination technique. The applications of the techniques for the determination of 4th WL substances are summarized in Table 2 in liquid samples and Table 3

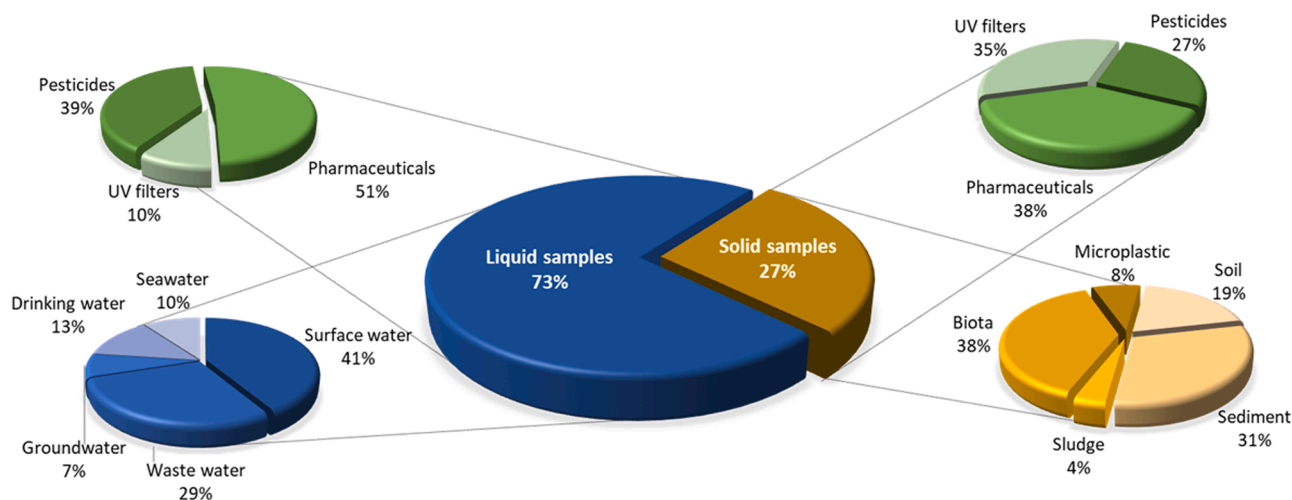


Fig. 2. Distribution of occurrence of contaminants from the 4th WL in different environmental samples.

in solid samples, and Fig. 3 shows the recovery percentages of WL compounds from various liquid and solid samples.

The combination of solid-phase extraction, high-performance liquid chromatography, and tandem mass spectrometry (SPE-LC-MS/MS) is currently the most widely used analytical method in this field [13–16]. In some cases, the authors used a more efficient separation with ultra-performance liquid chromatography (UPLC) instead of LC [17–20]. However, spectrophotometric UV, Vis or diode array detector (DAD) [21–23] and fluorescence detection (FLD) [24,25] can also be used. Gas chromatography with mass spectrometry (GC-MS) is a suitable alternative to LC-MS/MS for some substances such as fipronil, metconazole, metformin and tetraconazole [26–28]. GC-MS is considered a suitable alternative to LC-MS/MS for analysing volatile and semi-volatile compounds that can be easily vaporized. This makes GC-MS a valuable technique for substances with low molecular weights and high vapor pressures. In contrast, LC-MS/MS is generally preferred for compounds that are less volatile. Therefore, the choice between GC-MS and LC-MS/MS depends on the physical-chemical properties of the analytes.

Some articles focused on modern extraction techniques for example: dispersive liquid-liquid microextraction (DLLME) [24], hollow fiber solid-phase microextraction (HF-SPME) [29], salt assisted liquid-liquid microextraction (SALLME) [30], magnetic solid-phase extraction (MSPE) [31] etc. These modern extraction techniques are investigated with the goal of improving sensitivity, accuracy in analysis, reducing solvent use, and shortening extraction times. These methods align with green chemistry principles and reduce environmental impact.

In this section, the most appropriate extraction/preconcentration technique for each group of contaminants in each type of matrix, as well as the determination technique used in each case will be discussed.

2.1. Liquid samples

2.1.1. Pesticides

Pesticides occupy a large part of the new 4th WL, with 12 out of 25, which represents 48 % of the substances listed including fungicides, herbicides, insecticides, etc., mainly used in agriculture, which, after use, can reach surface or groundwater. Various extraction/preconcentration procedures have been optimized for each compound to enhance overall analytical performance and accuracy

Azoxystrobin is an example of a fungicide that has been extracted by using different techniques from water samples such as magnetic efferescent tablet-assisted ionic liquid dispersive liquid-liquid microextraction (META-IL-DLLME) [35], air-assisted liquid microextraction (AALLME) [32] or also via a passive sampler like Polar Organic

Chemical Integrative Samplers (POCIS) [34]. Regarding the recovery of the extraction technique, very good values of this parameter were obtained (between 82 – 104 %), probably because the procedures were optimized for a low number of contaminants (3–12) with similar properties [32,34,35]. When SPE with HLB cartridges is used as the extraction technique, high recovery results are observed. Regarding the use of a passive sampler like POCIS [34], the analyte concentration can increase over the exposure time. In this specific case, the sampler was deployed for 15 days. In relation to the matrix effect, it was mainly studied when MS/MS was used as a determination technique, since it is more influenced by interferences than DAD.

On the contrary, Medina et al. [33] found matrix effect when SPME-GC-MS was used, but it was not quantified. The LOD of the method can be influenced by several factors such as recovery or matrix effect, but in general a lower LOD is obtained when a higher enrichment factor is achieved. Nevertheless, in the case of azoxystrobin, the lowest LOD was obtained by POCIS, probably because it preconcentrates the analyte over time. After comparison of the detection techniques used, it is seen in general, that lower LODs were obtained using MS/MS compared to DAD, since it is a more sensitive technique.

Several methods were developed for the extraction/preconcentration of fipronil with different results as well. For instance, Wan et al. [38] extracted 1 L of water sample by Oasis HLB SPE cartridges obtaining a LOD of 10 ng L⁻¹, which may be considered high considering the preconcentration factor achieved and the absence of matrix effect. Same cartridges were also used by Shi et al. [5] who obtained a slightly higher LOD a bit higher (30 ng L⁻¹) probably due to the use of less volume of sample (only 500 mL). However, best LODs were obtained using online SPE (0.1 – 0.5 ng L⁻¹) [19] even though online SPE utilized smaller sample volumes (2 mL). In contrast, De Toffoli et al. [26] obtained an extremely high LOD (3100 ng L⁻¹) using SPE (500 mL) coupled with GC-MS, compared with previous papers that also used SPE HLB cartridges (Supelco Analytical). As happen with the previous compounds, most of the papers consulted obtained very good values of recovery using SPE Oasis HLB cartridges, except Supowit et al. [39] that obtained wide values of recovery (60 – 101 %) using SPE-GC-MS/MS with Strata X cartridges, also with a 500 mL sample, achieving similar LODs. The disparity in LODs may be attributed to factors such as differences in sample volumes or instrumental sensitivity.

A new methodology using magnetic SPE was applied by Liu et al. [7] for the analysis of ipconazole together with other 96 pesticides. LOD obtained with this approach (0.13 – 0.42 ng L⁻¹) were better than those obtained by SPE disk (LOQ = 20 ng L⁻¹) [4], but recovery was slight lower (75 – 95 % [4] and 72 – 79 % [7]). It could be also due to the difference in the number of compounds used in each work, which

Table 2
Analytical methods for substances from the 4th European watch list in liquid samples.

Analyte	Category	Sample	Number of analytes	Extraction technique	Analytical technique	Sensitivity	Recovery (%)	Matrix effect (%)	Ref.
Azoxystrobin	Pesticide	Surface water	3 (Pesticides)	AALLME	LC-DAD	80 ng L ⁻¹ (LOD)	82.3–103.0	n.l.	[32]
Azoxystrobin	Pesticide	Surface water	6 (Pesticides)	SPME	GC- μ ECD and GC-MS	30 ng L ⁻¹ (LOD) 50 ng L ⁻¹ (LOQ)	99.5–104.2	n.l.	[33]
Azoxystrobin	Pesticide	Surface water	7 (Pesticides)	POCIS	LC-MS/MS	0.1–2.1 ng L ⁻¹ (LOD) *	n.l.	n.l.	[34]
Azoxystrobin	Pesticide	Surface water	4 (Pesticides)	META-IL-DLLME	LC-DAD	20 ng L ⁻¹ (LOD)	98.1	n.l.	[35]
Diflufenican	Pesticide	Wastewater	2 (Pesticides)	DSPE	GC-MS	1400 ng L ⁻¹ (LOD) 4700 ng L ⁻¹ (LOQ)	99.5–104.7	33–106	[6]
Diflufenican	Pesticide	Surface and groundwater	69 (Pesticides)	SPE	LC-MS	87 ng L ⁻¹ (LOD) 204 ng L ⁻¹ (LOQ)	59.1	n.l.	[36]
Dimoxystrobin	Pesticide	Surface and drinking water	5 (Pesticides)	MSPE	LC-MS/MS	10 ng L ⁻¹ (LOD) 20–40 ng L ⁻¹ (LOQ)	81.8–109	n.l.	[31]
Famoxadone	Pesticide	Surface water and wastewater	3 (Pesticides)	SDME	LC-UV	190 ng L ⁻¹ (LOD) 630 ng L ⁻¹ (LOQ)	75.2–81.8	n.l.	[37]
Fipronil	Pesticide	Drinking and ground water	5 (Pesticide derivatives)	SPE	LC-MS/MS	0.02 ng L ⁻¹ (MDL) 10 ng L ⁻¹ (LOQ)	82–95	n.l.	[5]
Fipronil	Pesticide	Surface and drinking water	9 (Pesticides)	Online SPE	LC-MS/MS	0.1–0.5 ng L ⁻¹ (LOD)	91–104	–5.1–2.7	[19]
Fipronil	Pesticide	Surface and drinking water	10 (Pesticides)	SPE	LC-MS-MS	10 ng L ⁻¹ (LOQ) 0.01 ng L ⁻¹ (MDL)	84.7–105	n.l.	[38]
Fipronil	Pesticide	Surface water	4 (Pesticide metabolites)	SPE	GC-MS	3100 ng L ⁻¹ (LOD) 10200 ng L ⁻¹ (LOQ)	100.93–106.95	n.l.	[26]
Fipronil	Pesticide	Wastewater	5 (Pesticide metabolites)	SPE	GC–EI–MS/MS and LC–ESI–MS/MS	0.05–0.77 ng L ⁻¹ (LOD)*	116	n.l.	[39]
Imazalil	Pesticide	Wastewater	17 (Pesticides)	SPE	LC-QqLIT/QTOF-MS/MS	1.4 ng L ⁻¹ (MDL) 3.1 ng L ⁻¹ (MQL)	81–89	6	[16]
Ipconazole	Pesticide	Surface water	18 (Antibiotics, pesticides and drugs)	SPE	LC-MS/MS	20 ng L ⁻¹ (LOQ)	95	n. l.	[4]
Ipconazole	Pesticide	Seawater	96 (Pesticides)	MSPE	LC-MS/MS	0.19 ng L ⁻¹ (LOD) 1.0 ng L ⁻¹ (LOQ)	72–79	1.1	[7]
Metconazole	Pesticide	Surface water	>250 (pesticides)	SPE	LC-Q-Orbitrap-MS	2.5 ng L ⁻¹ (LOQ)	67–83	–13	[15]
Metconazole	Pesticide	Drinking water	57 (Pesticides)	SPE	LC–MS/MS	6 ng L ⁻¹ (LOD) 20 ng L ⁻¹ (LOQ)	70–120*	n.l.	[20]
Metconazole	Pesticide	Surface water and seawater	34 (Pesticides)	DLLME	GC-MS	4.9 ng L ⁻¹ (LOD) 15 ng L ⁻¹ (LOQ)	91–96	n.l.	[27]
Penconazole	Pesticide	Surface water and groundwater	13 (Pesticides)	SPE	LC-QqQ-MS/MS	50 ng L ⁻¹ (MQL)	102.2–108.4	–12	[40]
Penconazole	Pesticide	Surface water and drinking water	4 (Pesticides)	SS-LPE	GC-MS	330 ng L ⁻¹ (LOD) 1100 ng L ⁻¹ (LOQ)	91.5–103.5	n.l.	[41]
Prochloraz	Pesticide	Wastewater	29 target compounds (Pesticides)	SPE	QqLIT-MS/MS and QTOF-MS/MS	0.1 ng L ⁻¹ (MDL) 0.6 ng L ⁻¹ (MQL)	83–103	8	[16]
Prochloraz	Pesticide	Surface water	252 (Pesticides)	SPE	LC-Q-Orbitrap-MS	2.5 ng L ⁻¹ (LOQ)	67–81	–13	[15]
Prochloraz	Pesticide	Surface water	21 (Pesticides)	Offline SPE	LC-MS/MS	0.8 ng L ⁻¹ (LOD) 6.0 ng L ⁻¹ (LOQ)	53	n.l.	[42]
Tebuconazole	Pesticide	Surface water	13 (Pesticides)	SPE	LC-MS/MS	5 ng L ⁻¹ (MDL) 25 ng L ⁻¹ (MQL)	77–96	94	[43]

(continued on next page)

Table 2 (continued)

Analyte	Category	Sample	Number of analytes	Extraction technique	Analytical technique	Sensitivity	Recovery (%)	Matrix effect (%)	Ref.
Tebuconazole	Pesticide	Surface water and groundwater	3 (Triazole pesticides)	AA-IL-DLLME-SA	LC-DAD	190–380 ng L ⁻¹ (LOD) 650–1260 ng L ⁻¹ (LOQ)	76.5–100.1	n.l.	[44]
Tebuconazole	Pesticide	Surface water	2 (Pesticide enantiomers)	QuEChERS	SFC-MS/MS	0.12–0.19 ng g ⁻¹ (LOD) 0.38–0.65 ng g ⁻¹ (LOQ)	79.8–104.7	–99.30– (–99.28)	[45]
Tetraconazole	Pesticide	Groundwater	15 (Pesticides)	SPE	LC-MS/MS	0.02 ng L ⁻¹ (LOQ)	52–82	n.o.	[46]
Clindamycin	Antibiotic	Drinking water	2 (Antibiotics)	GO-d-SPE	LC-UV	240 ng L ⁻¹ (LOD) 710 ng L ⁻¹ (LOQ)	94.2–98.6	n.l.	[17]
Clindamycin	Antibiotic	Surface water, wastewater, groundwater and drinking water	26 (Pharmaceuticals and metabolites)	SPE	HILIC-ESI-MS/MS	0.1–2 ng L ⁻¹ (LOQ) 0.5 ng L ⁻¹ (IQL)	102–148	29–179	[47]
Clotrimazole	Antifungal	Wastewater	16 (Antibiotics and antimycotics)	SPE	LC-MS/MS	0.01 ng L ⁻¹ (LOD) 0.03 ng L ⁻¹ (LOQ)	63.8–121.0	n.l.	[48]
Fluconazole	Antifungal	Surface water	67 (Pharmaceuticals and antifungals)	SPE	LC-Orbitrap-MS	1.6 ng L ⁻¹ (LOD) 5.0 ng L ⁻¹ (LOQ)	106.3	–5	[49]
Guanylurea	Transformation product of metformin	Surface water, wastewater and drinking water	5 (Pesticide transformation products)	Lyophilization	LC-QTOF	10 ng L ⁻¹ (LOQ)	70	n.l.	[50]
Guanylurea	Transformation product of metformin	Wastewater	2 (Antidiabetic and transformation product)	SPE	LC-UV-Vis/ESI/MS	4.6–9.8 ng L ⁻¹ (LOD) 14.1–28.3 ng L ⁻¹ (LOQ)	44.4–60.1	5.8	[51]
Metformin	Antidiabetic	Wastewater	14 (Emerging organic contaminants)	SPE	LC-Orbitrap-MS	500 ng L ⁻¹ (LOQ) (for 11 analytes)	4–24*	n.l.	[52]
Metformin	Antidiabetic	Wastewater and drinking water	25 (Pharmaceuticals)	SPE	LC-MS/MS	0.07–0.75 ng L ⁻¹ (MDL) 0.22–2.25 ng L ⁻¹ (MQL)	14.0–32.1	n.l.	[14]
Metformin	Antidiabetic	Wastewater	1 (Antidiabetic)	SPE	GC-MS	129 ng L ⁻¹ (LOD) 429 ng L ⁻¹ (LOQ)	90.2–119.6	112.6–116.1	[28]
Miconazole	Antifungal	Surface water	9 (Pharmaceuticals)	LTPE	LC-ESI-MS/MS	1.20 ng L ⁻¹ (LOD) 3.85 ng L ⁻¹ (LOQ)	90.26–110.20	7.9–37.4	[53]
O-desmethylenlafaxine	Metabolite of venlafaxine	Surface water	23 (Chiral drugs)	SPE	LC-MS/MS	0.03 ng L ⁻¹ (MDL) 0.09–0.1 ng L ⁻¹ (MQL)	n.l.	n.l.	[54]
Ofloxacin	Antibiotic	Surface water	42 (Pharmaceuticals)	SPE	LC-MS/MS	25 ng L ⁻¹ (LOD) 50 ng L ⁻¹ (LOQ)	106–141	n.l.	[23]
Ofloxacin	Antibiotic	Surface water	4 (Antibiotics)	SPME	LC-UV-Vis	6021 ng L ⁻¹ (LOD) 20020 ng L ⁻¹ (LOQ)	96.9–109.6	n.l.	[21]
Ofloxacin	Antibiotic	Surface water and drinking water	12 (Sulphonamides and quinolones)	MSPE	LC-UV	1000 ng L ⁻¹ (LOD) 3400 ng L ⁻¹ (LOQ)	88.1–101.0	n.l.	[55]
Sulfamethoxazole	Antibiotic	Surface water	2 (Antibiotics)	SPE	LC-UV/FLD/MS	10 ng L ⁻¹ (LOD) 30 ng L ⁻¹ (LOQ)	85–91	n.l.	[25]
Sulfamethoxazole	Antibiotic	Surface water	2 (Antibiotic and its metabolite)	SPE	LC-MS/MS	0.4 ng L ⁻¹ (LOD) 1.2 ng L ⁻¹ (LOQ)	85–91	n.l.	[56]

(continued on next page)

Table 2 (continued)

Analyte	Category	Sample	Number of analytes	Extraction technique	Analytical technique	Sensitivity	Recovery (%)	Matrix effect (%)	Ref.
Sulfamethoxazole	Antibiotic	Drinking water and wastewater	2 (Antibiotics)	MSPE	UV-Vis	31700 ng L ⁻¹ (LOD) 104000 ng L ⁻¹ (LOQ)	95.1	n.l.	[57]
Trimethoprim	Antibiotic	Surface water	7 (Sulphonamide antibiotics)	SALLME	LC-UV	119200 ng L ⁻¹ (LOD) 361100 ng L ⁻¹ (LOQ) 7640 ng L ⁻¹ (MDL)	101.12	n.l.	[30]
Trimethoprim	Antibiotic	Surface, ground water and wastewater	18 (Antibiotics)	Online SPE	LC-qOrbitrap	0.3 ng L ⁻¹ (MDL) 0.9 ng L ⁻¹ (LOQ)	84.3–110	n.l.	[58]
Venlafaxine	Antidepressant	Surface water, drinking water and wastewater	1 (Antidepressant)	DLLME	LC-FLD	24.2 ng L ⁻¹ (LOD)	76–93	n.l.	[24]
Venlafaxine	Antidepressant	Surface water and drinking water	2 (Antidepressant and its metabolite)	HF-SPME	LC-DAD	30 ng L ⁻¹ (LOD) 100 ng L ⁻¹ (LOQ)	86.4–90.1	n.l.	[29]
Venlafaxine	Antidepressant	Surface water	5 (Pharmaceuticals)	MIP-SPE	LC-QTOF	300 ng L ⁻¹ (LOD) 1000 ng L ⁻¹ (LOQ)	92.3–106.7	n.l.	[59]
Venlafaxine	Antidepressant	Surface water and wastewater	10 (Antidepressants and their metabolites)	SPE	LC-MS/MS	0.1 ng L ⁻¹ (LOQ)	n.l.	84–91	[60]
Benzophenone–3	UV filter	Surface water	5 (UV filters)	SPE	LC-MS/MS	40 ng L ⁻¹ (LOD)	67	n.l.	[61]
<u>Benzophenone–3</u>	<u>UV filter</u>	<u>Surface water</u>	<u>23</u> <u>(Benzothiazoles and UV filters)</u>	<u>SPE</u>	<u>GC-MS/MS</u>	<u>0.025 ng L⁻¹ (MDL)</u> <u>0.083 ng L⁻¹ (MQL)</u>	<u>110–139</u>	<u>n.l.</u>	[62]
Butyl methoxydibenzoylmethane	UV filter	Seawater	24 (UV filters and hormones)	SPE	LC-MS/MS	3.00 ng L ⁻¹ (LOD) 10.00 ng L ⁻¹ (LOQ)	n.l.	n.l.	[63]
Octocrylene	UV filter	Seawater	10 (Personal care products)	SPE	LC-MS/MS	1.0 ng L ⁻¹ (MDL) 2.0 ng L ⁻¹ (MQL)	97–108	2	[13]
Octocrylene	UV filter	Seawater and wastewater	8 (UV filters)	SPE	LC-MS/MS	12.7–45.6 ng L ⁻¹ (MDL) 42.4–152.0 ng L ⁻¹ (MQL)	50.6–89.5	n.l.	[64]
Octocrylene	UV filter	Seawater, surface and drinking water	11 (UV filters)	USAEME	GC-MS/MS	0.5 ng L ⁻¹ (LOD) 1.7 ng L ⁻¹ (LOQ) 50 ng L ⁻¹ (IDL)	86.4–105	n.l.	[65]

Table 3
Analytical methods for substances from the 4th European watch list in solid samples (soils, sediments, sludge, biota, plastics).

Analyte	Category	Sample	Number of analytes	Samples treatment	Analytical technique	Detection sensitivity	Recovery (%)	Matrix effect (%)	Ref.
Fipronil	Pesticide	Soil and sediment	4 (Pesticide metabolites)	UAE	GC-MS	7.8 ng g ⁻¹ (LOD) 25.5 ng g ⁻¹ (LOQ)	92.92–102.76 (sediment) 100.33–110.18 (soil)	n.l.	[26]
Fipronil	Pesticide	Biosolids	5 (Pesticide metabolites)	SLE SPE	LC–ESI–MS/ MS	0.02–0.24 ng g ⁻¹ (LOD)*	48–90*	n.l.	[39]
Metconazole	Pesticide	Soil	4 (Chiral pesticides)	QuEChERS	LC-MS/MS	0.0073–0.0303 ng g ⁻¹ (MQL)	92.34–103.59	86.37–99.28	[8]
Metconazole	Pesticide	Soils	10 (Pesticides and their enantiomers)	QuEChERS	LC-MS/MS	2.2–9.1 ng L ⁻¹ (IDL) 0.00023–0.00089 ng g ⁻¹ (MDL)	92.3–103.6	86.4–99.3	[66]
Metconazole	Pesticide	Soil	4 (Pesticide stereoisomers)	QuEChERS	LC-UV	240–590 ng g ⁻¹ (LOD) 1240–1860 ng g ⁻¹ (LOQ)	97.19–104.91	1.06	[22]
Prochloraz	Pesticide	Sediments	21 (pesticides)	QuEChERS	LC-MS/MS	0.67 ng L ⁻¹ (LOD) 2.00 ng L ⁻¹ (LOQ)	78	n.l.	[42]
Tebuconazole	Pesticide	Soils	13 (Pesticides)	QuEChERS DSPE	LC-MS/MS	0.1 ng g ⁻¹ (MDL) 0.4 ng g ⁻¹ (MQL)	95–103	92	[43]
Tebuconazole	Pesticide	Biota (Zebrafish)	2 (Pesticide enantiomers)	QuEChERS SPE	SFC-MS/MS	0.07–0.12 ng g ⁻¹ (LOD) 0.24–0.41 ng g ⁻¹ (LOQ)	84.1–108.4	–99.18– (–99.03)	[45]
Tetraconazole	Pesticide	Biota (catfish)	302 (Pesticides)	QuEChERS Micro-SPE	GC–MS/MS	5 ng g ⁻¹ (LOQ)	98–111	±20*	[10]
Tetraconazole	Pesticide	Soil, sediment and biosolids	167 (Pesticides)	PLE EDGE	LC-MS/MS	0.11 ng g ⁻¹ (MDL)	89.57	n.l.	[67]
Clindamycin	Antibiotic	Soils and sediments	45 (Pharmaceuticals)	PHWE SPE	LC-MS/MS	0.01 ng g ⁻¹ (MLD) 0.2 ng g ⁻¹ (MLQ)	55–109 (soil) 24–73 (sediment)	n.l.	[68]
<u>Clotrimazole</u>	<u>Antifungal</u>	<u>Microplastics and plastic debris</u>	<u>19</u> <u>(Biocides)</u>	<u>UAE</u> <u>SPE</u>	<u>LC-MS/MS</u>	<u>7.64 ng g⁻¹ (LOD)</u> <u>25.46 ng g⁻¹ (LOQ)</u>	<u>90–148</u>	<u>n.l.</u>	<u>[18]</u>
<u>Clotrimazole</u>	<u>Antifungal</u>	<u>Biota (fish)</u>	<u>6</u> <u>(Azole fungicides)</u>	<u>SLE</u> <u>LLE</u> <u>SPE</u> <u>UAE</u>	<u>LC-MS/MS</u>	<u>0.02–0.07 ng g⁻¹ (MDL)</u> <u>0.07–0.24 ng g⁻¹ (MQL)</u>	<u>40.6–52.9</u>	<u>–1–17–4.54</u>	<u>[69]</u>
Guanylyurea	transformation product of metformin	Biota (fish)	2 (Antidiabetic and its transformation product)	SLE SPE	CE-TOF-MS	34 ng g ⁻¹ (LOD) 101 ng g ⁻¹ (LOQ)	84	–52–23	[70]
Metformin	Antidiabetic	Biota (fish)	81 (Pharmaceuticals)	UAE DSPE	LC-Orbitrap-MS	0.01–0.99 ng g ⁻¹ (LOD) 0.05–3.31 ng g ⁻¹ (LOQ)	<20–64	–99–(–74)	[71]
Miconazole	Antifungal	Sediments	36 (Contaminants of emerging concern)	QuEChERS DSPE	LC-MS/MS	0.06 ng g ⁻¹ (LOD)	66–93	–15–(–18)	[9]
Sulfamethoxazole	Antibiotic	Biota (fish, mollusc and bivalves)	16 (Emerging organic contaminants)	QuEChERS SPE	LC-MS/MS	0.05 ng g ⁻¹ (MDL)	66–82	–20	[72]
Benzophenone–3	UV filter	Sediments	5 (UV filters)	SLE	LC-DAD	4.6 ng g ⁻¹ (LOD)	47	n.l.	[61]
Benzophenone–3	UV filter	Sediment	23 (Benzothiazoles and UV filters)	UAE-SLE	GC-MS/MS	0.51 ng g ⁻¹ (MDL) 1.71 ng g ⁻¹ (MQL)	82–109	n.l.	[62]
Benzophenone–3	UV filter	Soils and biota (plants)	12 (UV filters)	UAE	GC-MS	0.163 ng g ⁻¹ (LOD) for soil 0.727 ng g ⁻¹ (LOD) for plant 0.544 ng g ⁻¹ (LOQ) for soil 2.42 ng g ⁻¹ (LOQ) for plant	85.9 (plant) 106 (soil)	n.l.	[73]
Butyl methoxydibenzoylmethane	UV filter	Microplastic debris	12 (UV filters and stabilisers)	UAE	LC-MS/MS	0.13 ng g ⁻¹ (LOD) 0.43 ng g ⁻¹ (LOQ)	n.l.	n.l.	[12]
Butyl methoxydibenzoylmethane	UV filter	Sediments and biota (coral tissue)	24 (UV filters and hormones)	QuEChERS reverse-SPE	LC-MS/MS	0.05–12.12 ng g ⁻¹ (LOD) 0.16–40.0 ng g ⁻¹ (LOQ)	n.l.	n.l.	[63]
Octocrylene	UV filter	Biota (mussels)	10 (Personal care products)	QuEChERS	LC-MS/MS	1.0 ng L ⁻¹ (MDL) 2.0 ng L ⁻¹ (MQL)	97–108	2	[13]

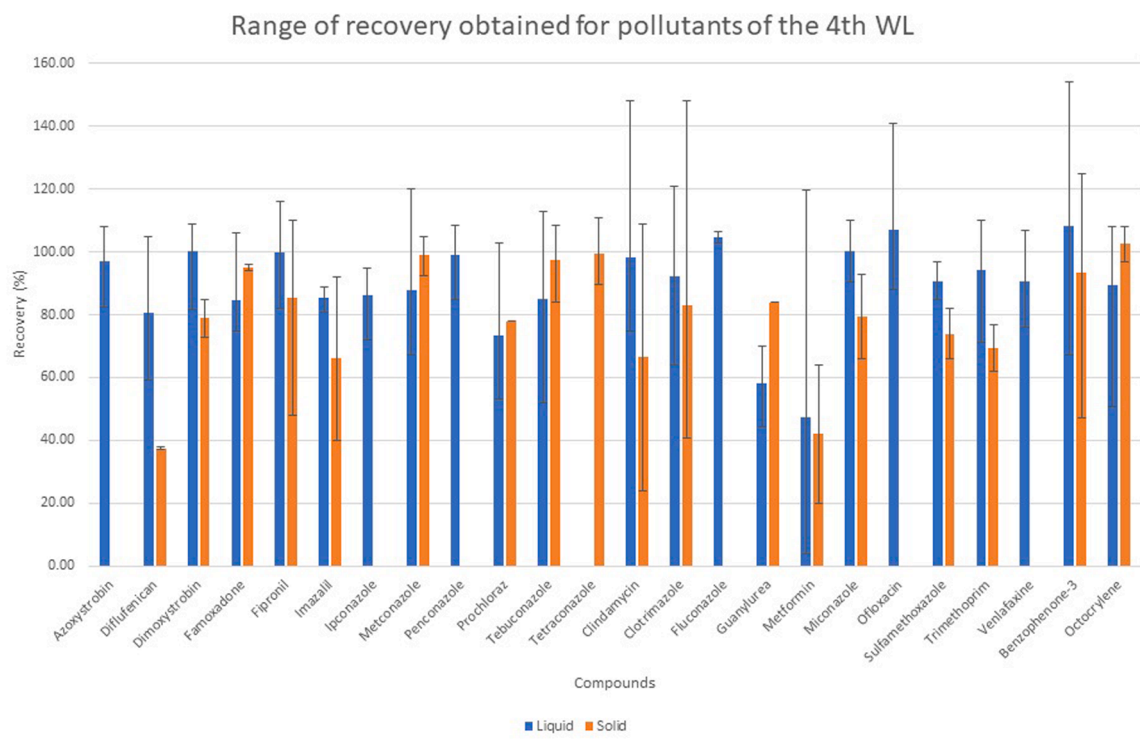


Fig. 3. Recovery percentages of 4th WL compounds from liquid and solid samples.

perhaps made the authors must make a compromise solution. QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe), using MgSO_4 and SiO_2 as adsorbents, were also used for the extraction of this pesticide from wastewater, obtaining a LOD close to the values obtained by SPE (4.9 ng L^{-1}) and better recovery (83 – 94 %), although suppression of the signal due to the matrix was observed. Differences in matrix effect probably were related with the complexity of wastewater compared to seawater [7] or surface water [4].

DLLME has been also used in the extraction of the fungicide metconazole prior its determination by GC-MS [27] obtaining a low LOD (4.9 ng L^{-1}), in range of those results obtained by LC-MS/MS (6 ng L^{-1}) [20] and with LC-Orbitrap ($\text{LOQ} = 2.5 \text{ ng L}^{-1}$) [15]. However, recoveries ranging from 91 – 96 % were obtained with DLLME, better than the results obtained by SPE with Oasis HLB cartridges (70 – 120 %) [20] and (67 – 95 %) [15]. Nevertheless, it must be considered the big number of compounds analyzed by Casado et al. [15].

Contrary to previous pesticides, penconazole has mainly been determined by GC-MS [41], with SS-LPE extraction technique. It has been found that all of them share good recovery with values 91 – 103.5 %. However, when the extraction and determination were done by SPE-LC-MS/MS [40], the recovery was 102 – 108.4 % and a the sensitivity was significantly better with MQL of 10 ng L^{-1} , compared to 330 ng L^{-1} [41] where GC-MS was employed

Prochloraz was extracted in all cases by SPE, although with different recovery in spite of using the same Oasis HLB cartridge (83 – 103 % [16] and 67 – 81 % [15]). However, as it was mentioned before, differences in recovery may be due to the need of adopting a compromise solution for all target analytes. LOD obtained by all authors were similar in their determination by LC-MS/MS.

For the extraction of tebuconazole, three different extraction techniques, SPE [43], AA-IL-DLLME-SA [44] and DSPE-LLE [45], were used with practically the same recovery results (77 – 96, 76.5 – 100.1 and 79.8 – 104.7, respectively). However, when using SPE with Oasis HLB cartridge the LOD was much lower (5 ng L^{-1} [43] versus $190\text{--}380 \text{ ng L}^{-1}$ [44] or $120\text{--}190 \text{ ng L}^{-1}$ [45]), probably due to the bigger volume of sample used in SPE. Furthermore, for this compound a

strong matrix effect was observed when MS/MS was used as determination technique even when the same matrix was used [43,45].

Among the pesticides of the 4th WL, some of them were found to be barely studied and difficult to compare, as is the case of difluenican. Only one extraction procedure has been optimized for this analyte [6], using DSPE as extraction technique and GC-MS as determination technique. Results were very good in terms of recovery, but LOD obtained was very high (1400 ng L^{-1}). Dimoxystrobin has been extracted only by microextraction techniques like MSPE [31], with range of recovery 82 – 109 %. LOD was also very different, however it could be due to the determination technique, since in most of cases MS/MS has more sensitivity than DAD. Famoxadone has been barely studied as well. Amde et al. [37] optimized an extraction method based on SDME before its determination by LC-UV. With both procedures good recoveries were achieved (75 – 81 % and 75 – 106 %, respectively), but Orbitrap showed better LOD (50 ng L^{-1}) than DAD (190 ng L^{-1}). The fungicide imazalil was extracted by ultrasound-assisted emulsification micro-extraction (USAEME) obtaining good results in terms of recovery (92.9 %) and LOD (0.2 ng L^{-1}), despite using DAD as detection system [74]. Very similar results were obtained using SPE and LC-MS/MS, achieving a recovery of 86 % and a LOD of 0.3 ng L^{-1} , with the added difficulty of working with many compounds (51).

2.1.2. Pharmaceuticals

Antibiotics also have a strong presence in the new 4th WL. Clindamycin has mainly been extracted with SPE [47]. Nejad et al. [17] developed a different approach using GO-d-SPE and obtaining very good values of recovery (96 – 102 %) compared to the previous ones with SPE (102 – 106 %) [47]. However, LOD obtained by Nejad et al. [17] (240 ng L^{-1}) was higher than with SPE procedures ($0.1\text{--}2 \text{ ng L}^{-1}$, [47] respectively). It could be due to the use of a different detector (UV) that is less sensitive than MS/MS. Regarding matrix effect, and despite using MS/MS, very different values were published by Boulard et al. [47], who obtained a wide range of matrix effect (29 – 178 %).

Regarding ofloxacin, only two papers using UV and one using MS/MS as detector have been reported; however, LOD obtained by UV was

far higher (1000 [55] and 6021 ng L⁻¹ [21]) than using MS/MS (25 ng L⁻¹) [23]. Recovery values were similar despite using different extraction procedure: MSPE (98 %) [55], SPME (97 – 110 %) [21] and SPE (106–141 %) [23].

Also, the determination of sulfamethoxazole has mainly been performed by LC-UV [25,57], with great differences regarding the LOD, ranging from 10 ng L⁻¹ [25] to 31700 ng L⁻¹ [57]. These differences could be attributed to the extraction technique, since all three authors used a different procedure: SPE [25] and MSPE [57]. Given that the recovery obtained was high in all cases, the use of SPE seems to be the best option [40] because, when it was used, much lower LODs were obtained (10 ng L⁻¹ [40] and 0.4 ng L⁻¹ [83]) compared to those obtained with MSPE (31700 ng L⁻¹ [84]) and MASPE (500 ng L⁻¹ [85]). LC-MS/MS was also used after SPE for the determination of sulfamethoxazole [56] obtaining the lowest LOD (0.4 ng L⁻¹).

The last antibiotic of the 4th WL is trimethoprim, for which a novel extraction method (SALLME) was also optimized [30]. In this case, UV was used as detector combined to LC, obtaining a LOD higher (7640 ng L⁻¹) [30] compared to that found with Orbitrap detection (0.3 ng L⁻¹) [58]. Regarding recovery, SALLME procedure did not offer neither a great improvement respect to SPE, since range of recovery was 87 – 115 % with SALLME [30] and 84 – 110 %, when SPE was used [58].

Other pharmaceuticals present in the 4th WL are antifungal, antidiabetic and antidepressants. Among the antifungals, only one extraction method has been optimized for miconazole; LTPE [53], with very good recovery results (90 – 110 %). Similar results were obtained for other antifungals, fluconazole, but using SPE 106 % [49]. Regarding the LOD, on all occasions MS/MS or HRMS was used, so low LOD were obtained ranging from 1 – 1.6 ng L⁻¹ [49,53].

The antidiabetic metformin and his transformation product, guanilurea, has mainly been extracted by SPE, obtaining a wide range of results probably due to the polarity of these analytes that make them difficult to retain in SPE cartridges. For instance, recovery obtained for guanilurea ranged from 44 – 60 % [51] which are lower than the results of Tisler & Zwiener [50] when used lyophilization (70 %). Metformin also presented very low recovery when it was intended to be extracted by SPE with Oasis HLB cartridge (4 – 24 % [52] and 14 – 32 % [14]). In contrast, Yan et al. [28] obtained good values of recovery (90 – 120 %) using Strata-X-CW cartridges. On the other hand, LOD obtained by Yan et al. [28] using GC-MS were considerably higher (129 ng L⁻¹) compared to those obtained by LC-MS/MS (0.07 – 0.75 ng L⁻¹ [14]). However, higher LOD were obtained using Orbitrap (500 ng L⁻¹ [52]).

The antidepressant venlafaxine and its metabolite O-desmethylvenlafaxine have been also studied, although the latter only in one work, achieving MDL of 0.03 ng L⁻¹ when SPE-LC-MS/MS was used [54]. Regarding venlafaxine, several extraction and determination techniques were used. Thus, new approaches in extraction and pre-concentration showed good values of recovery, especially when using microextraction techniques (76 – 93 % with DLLME [24] and 86 – 90 with HF-SPME [29]). In the case of venlafaxine determination, higher LOD value was obtained using QToF (300 ng L⁻¹) [59] than optic detectors such as FLD (24.2 ng L⁻¹) [24] or DAD (30 ng L⁻¹) [29].

2.1.3. UV filters

In relation to UV filters, octocrylene stands out above all of them. To analyze it, in most of papers SPE and LC-MS/MS have been used obtaining varied results of recovery (51 – 90 % [64] and 97 – 108 % [13]) and LOD (12.7 – 45.6 ng L⁻¹ [64] and 1 ng L⁻¹ [13]). In these occasions, results were improved when USAEME was used as extraction technique prior GC-MS/MS [65], obtaining a recovery ranging from 86 – 105 % and a LOD of 0.5 ng L⁻¹.

Regarding benzophenone-3, it was also analyzed by LC-MS/MS [61] and GC-MS/MS [75] obtaining practically the same LOD (1.3 ng L⁻¹); however, in spite of using SPE in both study, recovery results were different due to the type of cartridge (67 % [61] and 91 % [75]), achieving better results with Oasis HLB cartridges than with HyperSep™

phenyl.

In summary, most of the selected work was based on the optimization for a few contaminants, which traditionally leads to good recovery results. Microextraction techniques usually obtain better recovery values than SPE, but with a worse preconcentration or enrichment factor which in many cases involves a higher LOD. Among the cartridges used, oasis HLB continues to be the preferred one by the scientific community. Analysing the LOD to establish the best determination technique is very complicated, since it depends a lot on the work and/or the compounds analysed. However, MS/MS or HRMS usually have greater sensitivity than optical techniques, even though they are more susceptible to suffering matrix effect. In this sense, it was found that in many optimizations and validations of methods the matrix effect was not study.

2.2. Solid samples

Unlike studies in liquid samples, in which wastewater and surface water were mainly studied, and the extraction was mainly carried out by SPE, in solid samples very different matrices such as sediments, plants, algae, fish, soil, sludge, microplastics, etc. may be found. This fact means that the techniques used for extraction were more diverse, and, furthermore, the number of published works was smaller, making their comparison more complicated.

2.2.1. Pesticides

Among the pesticides of the 4th WL, several of them were studied only in one work: diflufenican, dimoxystrobin, famoxadone, imazalil, miconazole and prochloraz. The matrices analysed were also different: biota, sediment, soil, sludge, etc. (Table 3). and the extraction techniques used: QuEChERS, SLE and DSPE (Table 3); so, a comparison between the works was not possible.

Clotrimazole is an antifungal that has been analysed in fish and MPs. In both cases, UAE was used as extraction technique, followed by SPE as clean-up step. The differences in the matrix cause the recovery in fish (40–50 %) [69] to be much lower than in MPs (90–148 %) [18], although the matrix effect found in the fish was very low (3.8 %). Furthermore, the MDL obtained in the first work (0.06 ng g⁻¹) [69] is much better than the LOD obtained in MPs (7.64 ng g⁻¹) [18]. Fipronil was extracted using two different techniques, UAE [26] and SLE [39], obtaining much better recovery results using UAE (93 – 110 %) [26] than SLE (48 – 90 %) [39], although the LOD was better when LC-MS/MS was used (0.02 – 0.24 ng g⁻¹) [39] compared to GC-MS/MS results (7.8 ng g⁻¹) [26].

Metconazole is a pesticide that has been studied in soils by different authors, although all of them used QuEChERS for its extraction, achieving very good values of recovery in all cases, ranging from 92 % [8,66] to 105 % [22]. Extremely low MQL were obtained when LC-MS/MS was used as determination technique (0.0002 – 0.0009 ng g⁻¹ [66] and 0.007 – 0.03 ng g⁻¹ [8]), especially compared to LC-UV (240 – 590 ng g⁻¹) [22] and taking into account the high matrix effect in LC-MS/MS (86 – 99 %) [8,66]. Tebuconazole, another pesticide, was extracted from soils and zebrafish using QuEChERS as well. For this compound, very good recoveries were obtained with this technique, ranging from 95 – 103 % in soils [43] and from 84 – 108 % in biota [45]. Good MDL were obtained in soils (0.1 ng g⁻¹) [43] and better were obtained in biota (0.07 – 0.12 ng g⁻¹); however, matrix effect was higher in biota (-99 %) than in soil (92 %). Finally, tetraconazole was extracted from biota using QuEChERS [10], as above-mentioned fungicides, but a different approach was also optimized using EDGE for its extraction from soil, sediment and biosolids [67]. Recovery obtained with this approach (90 %) [67] was similar to those obtained by QuEChERS (98–111 %) [10]; however, LOQ was higher (5 ng g⁻¹) when QuEChERS combined with GC-MS/MS was used [10] than EDGE with LC-MS/MS (0.11 ng g⁻¹) [67].

2.2.2. Pharmaceuticals

Several pharmaceuticals have been extracted from solid matrix, highlighting fish. However, these compounds were studied on few occasions to draw conclusions. Among them, the extraction procedure for clindamycin is worth mentioning due to the extraction method employed (PHWE) [68]. Wide range of recovery was obtained (55 – 109 %) using this technique; however, it was in accordance with the rest of the procedures (Table 3). For the determination of the pharmaceuticals, LC coupled to MS/MS or HRMS was used in all cases, except in the determination of guanlyurea [70], which used CE for its separation. In this work, a significantly higher LOD was obtained than the others (Table 3), suggesting that LC is a better separation technique that allows better detection. Nevertheless, due to the polarity of this compound, applying and testing other separation techniques is very convenient.

2.2.3. UV filters

Three UV filters have been studied in solid matrix: benzophenone-3, butyl methoxydibenzoylmethane and octocrylene, although the last one in only one occasion. Benzophenone-3 was the most studied compound. Its extraction was performed mainly by solid-liquid extraction, normally assisted by ultrasounds (UAE), in the different matrix (sediments, soils, plants, sludge, etc.). In most of cases the recovery achieved was close to 100 % (Table 3), except in one work (47 %) in sediments [61]. Previous paper was also the only one that used LC-DAD for the determination of benzophenone-3, since it was mainly determined by GC-MS/MS. Among all papers summarized in Table 3, MDL or LOD were in the same range. Butyl methoxydibenzoylmethane was determined in MPs [12], sediments and biota [63]. In both cases LC-MS/MS was used as determination technique, leading to LOD values ranging from 0.13 ng g⁻¹ [12] to 12 ng g⁻¹ [63], probably due to MPs are a cleaner matrix than biota.

In summary, the extraction of contaminants present in solid samples is more complicated than in liquid samples, involving different extraction techniques and usually cleaning steps. In general, it can be concluded that the most used extraction techniques and that presents the best recoveries are QuEChERS for biota and UAE for soils and sediments. Likewise, MS/MS is the most common detection system which provides the lowest LODs. However, many works fail to specify the matrix effect, which is one of the main disadvantages of this technique.

Regarding the extraction of pollutants from MPs, it has been found that the target compounds can be extracted using UAE with the same efficiency as Soxhlet extraction or other conventional techniques. UAE offers the advantages of reducing extraction time and minimizing the use of organic solvents.

3. Watchlist compounds adsorbed on microplastics

The term "microplastics" (MPs) was officially coined in 2004 drawing attention to the escalating issue of plastic pollution in the oceans. Subsequently, its prevalence in the environment has garnered growing concern from scientists, authorities, the general population, and the media. While there is no universally accepted definition among authors, microplastics are commonly described as plastic fragments measuring less than 5 mm in any dimension, with an undefined lower limit. Nowadays, MPs have already been ubiquitous reported in almost all aquatic habitats of the planet, from the open seas to deep oceans, rivers, lakes, the water column, and sediments and in other environmental compartments [76]. Microplastics and other pollutants coexist in the environment, raising growing concerns due to their simultaneous presence. MPs, known for their high sorption capacity, have been reported to function as carriers of pollutants [77]. The ingestion of contaminated MPs by organisms can exacerbate the desorption of pollutants, amplifying their bioavailability and toxicity [78]. Understanding the behaviour and sorption mechanisms between naturally modified microplastics and organic contaminants is crucial for evaluating their true impact on the environment [79]. In this context, the study of adsorption of recent organic compounds from the 4th WL constitutes an important

contribution in this field.

3.1. Factors influencing adsorption behavior and sorption mechanisms of microplastics

The factors influencing the adsorption of organic pollutants (OPs) on microplastics could be categorized into three distinct groups [80]. The first group pertains to the impact of microplastics (MPs) properties on their adsorption capacity. The type of MPs plays a crucial role in various factors, including polarity, size, crystallinity, and functional groups. Environmental factors, such as weathering and aging, will influence MPs properties too. The physicochemical characteristics of the organic contaminants themselves can be included in the second group of influencing factors. Additionally, the third category is the environmental conditions, including temperature, pH, and salinity, also play a role in affecting the adsorption capacity of MPs. Fig. 3 provides a summary of how these factors collectively influence the adsorption capacity of MPs [80].

3.1.1. Microplastics properties

Microplastics originate from a diverse range of polymer resins, each possessing distinct physical and chemical properties. There are different MPs types, according to their polymer composition: non-polar types include Polystyrene (PS), polypropylene (PP), and polyethylene (PE) while polar types include polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polyamide (PA) being considered strongly polar [81]. MPs possess a relatively large specific surface area, allowing them to adsorb organic pollutants on their surface. Thus, Polyethylene exhibits the highest surface area, followed by PS, PVC, and PP [82].

While particle size plays a relatively minor role compared to other factors, it can still influence adsorption rates and capacity [83]. Smaller particle generally offers more adsorption sites enhancing their capacity to adsorb pollutants. It was proven in several articles, that sorption capacities of all particles followed the size trend, despite differences in polymer composition.

In the natural environment, plastic polymers typically exhibit a combination of crystalline and amorphous regions. The crystalline region has a regular molecular possesses strong cohesion and compressibility, while the amorphous region is irregular and loose, resembling a viscous liquid [80]. The amorphous region of MPs attract organic pollutants more strongly than the crystalline region, indicating that higher crystallinity reduces adsorption capacity [84].

Recent studies show that MPs undergo aging and weathering processes that affect their adsorption capabilities. Environmental factors like UV radiation, water, and temperature alter their surface structure and introduce oxygen-containing functional groups [135,136]. This leads to a shift from hydrophobic to hydrophilic surfaces, enhancing the adsorption of hydrophilic organic pollutants [137]. Additionally, oxidation causes chain scission, expanding the amorphous region and improving the diffusion and sorption of organic pollutants [138].

3.1.2. Properties of the organic pollutants

MPs adsorb contaminants from their surrounding environments, with hydrophobicity being a key factor in sorption [85]. Initial research focused on studying the adsorption on MPs for hydrophobic organic pollutants (OPs), as they have suspect that to be the main substances adsorbed. However, environmental factors, can create oxygen-containing functional groups on MPs, leading to significant adsorption of hydrophilic OPs as well [77].

Contaminants are classified based on their octanol-water partition coefficient (K_{ow}). Compounds with log K_{ow} < 3 are classified as weakly hydrophobic or hydrophilic; those with 4 ≤ log K_{ow} ≤ 5, are moderately hydrophobic and strongly hydrophobic for log K_{ow} > 5 [27].

$$K_{ow} = \frac{(\text{solute})_{\text{octanol}}}{(\text{solute})_{\text{water}}}$$

Many researchers have studied the mechanisms of adsorb OPs by MPs. In general, compounds having high $\text{Log}K_{ow}$ (>3) are more easily absorbed by MPs through hydrophobic interactions [86]. However, compounds like metformin and guanylurea, due to their high hydrophilicity and polarity, have a low affinity for sorption onto MPs. This low affinity suggests that these compounds are less likely to be transported by microplastics in the environment. In contrast to this, pore filling, electrostatic forces, hydrogen bonding, and π - π bond interactions, play a crucial role in the behaviour and interactions of organic contaminants with hydrophilic and polar groups in their structure [78].

The distribution coefficient (K_d) characterizes the adsorption capacity of OPs on MPs. Thus, K_d values of the hydrophobic compounds are positively correlated with their octanol-water partition coefficients. For instance, less polar and non-ionic compounds exhibited a higher K_d value than polar compounds. Wu et al. [85] observed that the partitioning of more hydrophobic pharmaceuticals on polyethylene (PE) exhibited a linear relationship, which was directly correlated with their distribution coefficient values. The K_d values ranged between 191 and 53,225 L kg^{-1} for carbamazepine and 4-methyl benzylidene camphor, respectively, aligning with their respective hydrophilicities.

When the surface functional groups of MPs change, they can adsorb more polar substances through different mechanisms such as electrostatic interaction, π - π interaction, hydrogen bonding, and van der Waals force. Electrostatic interactions depend on the surface charges of MPs and OPs. This dependency is particularly influenced by the environmental pH [86]. π - π interaction, occurs between molecules with π -conjugated structure, but other functional groups can also affect their intensity. Hydrogen bonds predominantly form between polar polyamide (PA) and hydrophilic organic pollutants, such as antibiotics, or between MPs with halogen atoms (e.g., PVC) and organic compounds like PCBs and DDT. Also, MPs, such as PE, PP and PS can adsorb OPs (pharmaceuticals and PAHs) through Van der Waals forces. However, since the van der Waals forces are weak, the adsorbed OPs can be easily desorbed from the MPs when the environmental conditions change [87].

Adsorption often involves multiple interactions, adding complexity [88]. There is limited research on this topic. Gong et al. [89] found higher adsorption capacity of fipronil on biodegradable MPs, such as polylactic acid (PLA) and PBS, compared to non-degradable MPs (PE, PS, PVC, and PP). This difference was attributed to the stronger hydrogen bond interaction between fipronil and the carbonyl groups in degradable MPs. Fig. 4. 5 shows the potential interaction mechanisms between the OPs and MPs.

3.1.3. Environmental conditions

Exposure to natural conditions in aquatic environments can induce alterations in MPs, including heightened surface oxidation and the formation of micro-cracks, particularly evident in aged plastic. Kinetic models and isotherms have revealed that the sorption capacity of MPs subjected to natural modification processes surpasses that of pristine MPs [79].

Electrostatic interactions play a crucial role in sorption processes between microplastics and contaminants, influenced by their surface charges and environmental pH [90]. Typical aquatic pH levels ranging from 5 to 9, and changes in pH affect the ionization state of both the MPs and the OPs, altering their affinity for each other. MPs tend to aggregate in aquatic environments, a process controlled by surface charges and pH conditions.

Weathering processes generally increase the negative charges on the surface of MPs, enhancing the cationic sorption process. However, the effect of weathering to electrostatic interaction is limited, as the equilibria of other contaminants also depend on pH, thereby influencing the sorption capacity and rate [90]. Wan et al. [91] observed a gradual improvement in the adsorption of TCS, primarily in cationic form, by negatively charged PS-MPs as pH increased from 2.0 to 7.0. Following, an increase in pH from 7.0 to 9.0, the adsorption capacity gradually decreased. Overall, pH variations primarily influence sorption capacity

rather than structural modifications of MPs.

Salinity, temperature and dissolved organic matter (DOM) also significantly affect the sorption behaviour of organic pollutants to microplastics. Salinity can alter the electrostatic interactions and ion exchange. Liu et al. [90] observed that elevated salinity levels led to a higher concentration of Na^+ , which competes strongly with the cation exchange sites on the surface of MPs. This competition ultimately results in a reduction in the adsorption of OPs. Nevertheless, a distinct phenomenon was observed by Llorca et al. [92], indicating that elevated salinity can induce the salting-out effect of organic pollutants in solution. This results in a reduction of OPs solubility and promotes their adsorption onto MPs.

Temperature affects the adsorption process mainly by changing the structure of MPs, the solubility of OPs, and the interaction between them. Generally, elevated temperatures increase the solubility of OPs and reduce the adsorption energy enhancing the adsorption. A notable increase in the adsorption affinity for antibiotic contaminants was observed at temperatures above 45 °C compared to below 0 °C [93]. In contrary, Li et al. [94] showed that the adsorption of TCS on PS-MPs had no significant relationship with temperature, considering the ambient temperature was in the range of 15–45 °C.

Regarding DOM, at increased concentrations, this leads to a reduction in sorption onto MPs due to competitive interactions for binding sites and complexation with humic and fulvic acids, altering the partitioning equilibrium between the solid surface and the water phase [83].

3.2. Sorption kinetics and isotherms

The organic pollutant sorption capacity of microplastics was found to be approximately two to six orders of magnitude higher than that of sediments and seawater in previous studies. Sorption is the process of transferring chemicals from fluids (liquids and gases) to solids and includes adsorption and absorption [87]. During adsorption, chemical molecules are confined to the solid-liquid interface, while they penetrate the solid matrix during absorption. It is impossible to distinguish between adsorption and absorption because the two processes usually occur simultaneously [87]. When the concentration of organic pollutants in the environment is low, adsorption appears to be the predominant phenomenon, while at high concentrations, absorption primarily occurs.

Adsorption kinetic models assess pollutant adsorption on MPs, determining efficacy and rate-limiting steps. Typically, kinetics involve four stages: bulk transport (fast), film diffusion (slow), intraparticle diffusion (slow), and adsorption attachment (fast) according Ho et al. [95]. Key models include pseudo-first order, pseudo-second order, intraparticle diffusion, and film diffusion. Pseudo-first order and pseudo-second-order models assess overall adsorption, while intraparticle and liquid film diffusion models elucidate limiting steps. For complex mechanisms, intraparticle and liquid film diffusion models provide further insights beyond pseudo-first order and pseudo-second-order models according to Fu et al. [80].

In most instances, the pseudo first-order model proves suitable for describing the adsorption process of OPs onto MPs within the initial 20–30 minutes. This initial phase of adsorption is primarily influenced by physical diffusion. However, some studies have shown that the pseudo-second-order model performs better than the first order model in describing the adsorption kinetics of OPs on MPs [96]. For example, the adsorption of chlorophenol (CP) on polyethylene terephthalate (PET) MPs [97].

Regarding adsorption isotherms, they elucidate the equilibrium behaviour of adsorbents at constant temperature, taking into account the characteristics of the adsorbate, the adsorbent, and the properties of the adsorption solution, which encompass pH, ionic strength, and temperature [90]. These isotherms play a fundamental role in predicting the amount of adsorbate that can adhere to a solid surface and in discerning whether the adsorption mechanism aligns with linear monolayer

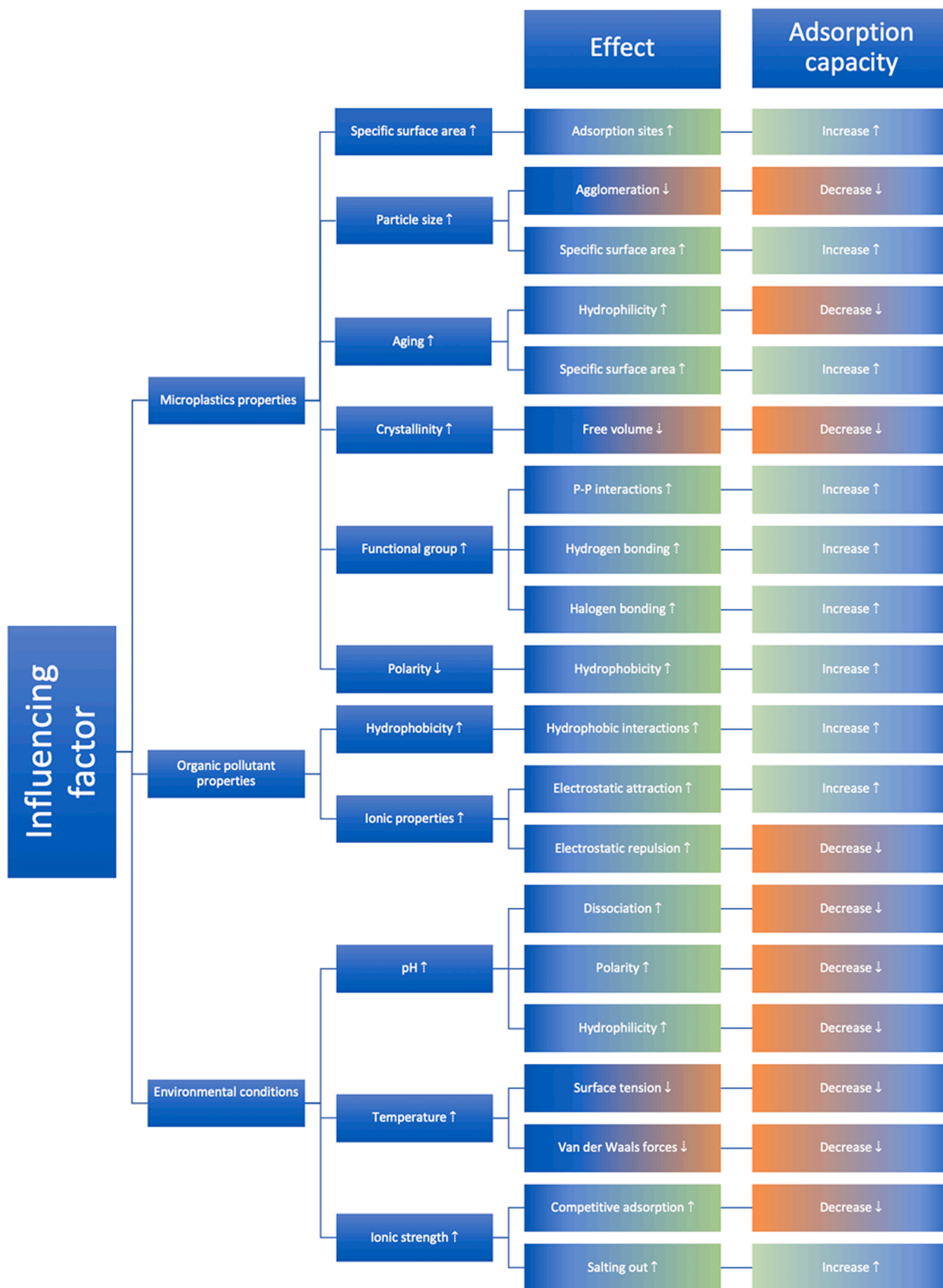


Fig. 4. Factors affecting the adsorption capacity of MPs [88].

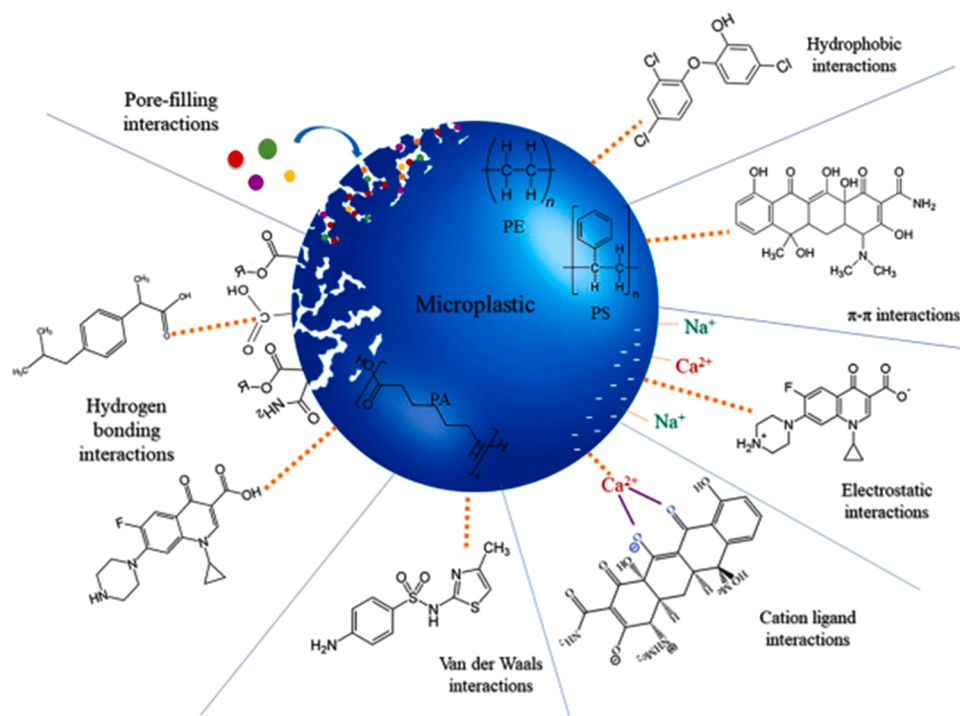


Fig. 5. Different types of interface interactions between OPs and MPs surface.

coverage or involves multilayer adsorption [79]. Common adsorption isotherm models include the linear isotherm, Langmuir, and Freundlich models. The Langmuir and Freundlich models are known to exhibit a higher degree of fit.

For a linear isotherm, the sorption distribution coefficient (K_d) represents the ratio between the concentration in the solid phase and the equilibrium concentration in the liquid phase. However, the relationship between solid and liquid phases may exhibit nonlinearity, necessitating the application of alternative models.

Langmuir isotherm is employed for homogeneous surfaces, describing a scenario in which the sorbate forms a monolayer with a finite number of sorption sites. The Langmuir model postulates a uniform surface of the adsorbent, assumes no interaction among adsorbents, and posits that adsorption solely transpires on the outer surface of the adsorbent, forming a monolayer [91]. The separation coefficient (k_1) within the Langmuir model serves as a crucial parameter for characterizing adsorption behavior. A k_1 value below 1 indicates preferential adsorption in the context of organic pollutants onto MPs.

Conversely, the Freundlich isotherm characterizes sorption onto heterogeneous surfaces, where high-energy sites are preferentially occupied and modeling of both monolayer (chemical adsorption) and multilayer adsorption (Van der Waals adsorption) scenarios. Within the Freundlich model, the adsorption coefficient k_f is used to describe the partitioning of organic pollutants between the surrounding aqueous solution and MPs, which largely depend on interactions between organic pollutants and MPs [77]. The parameter $1/n$ in the Freundlich model serves as an indicator of adsorption intensity or surface heterogeneity, revealing that adsorption diminishes as the sorbate concentration rises due to the limited availability of sites on the adsorbent for further sorption [90].

4. Occurrence in the environment

Based on the publications presented in previous sections, a detailed data analysis was conducted, focusing on the occurrence of contaminants from the 4th WL in various kind of liquid or solid environmental samples, such as surface water, wastewater, groundwater, drinking

water and seawater, and the solid samples are soil, sediment, sludge, biota, and microplastics. Of the total works listed in Tables 2 and 3, slightly more than half was devoted to the analysis of environmental samples, approximately 68 % for liquid samples and 27 % for solid samples.

4.1. Liquid samples

Azoxystrobin is frequently analyzed in surface waters such as rivers, lakes, lagoons, and reservoirs. High occurrence of azoxystrobin has been recorded in southern Brazil in 78 % of analyzed samples, with a maximum concentration of 2474 ng L⁻¹. Its presence has also been detected in rivers and lake in Argentina with relatively low concentrations ranging from 11.1 to 61.9 ng L⁻¹ [34]. Conversely, higher concentrations of azoxystrobin ranging from table 0–4260 ng L⁻¹ were found in water samples used for irrigating rice fields in Argentina [33]. These levels exceed the maximum residue limit (MRL) established by European Union legislation of 100 ng L⁻¹ by approximately 5–42 times. Fipronil was the most frequently detected target analyte in wastewater, groundwater, and drinking water. Its presence was reported in 65.1 % of drinking water samples and 75.5 % of groundwater samples in China, with concentrations ranging from n.d. to 0.9 ng L⁻¹ [5]. Other studies have reported its presence in industrial wastewater (28 ng L⁻¹) [39], drinking water from Montreal (5 ng L⁻¹) [19], or lake water samples from northern Vietnam (15.9 ng L⁻¹) [38]. In all these cases, fipronil concentrations exceeded either the chronic benchmark value of 11 ng L⁻¹ established in the United States or the threshold value of 0.07 ng L⁻¹ established in the Netherlands [98]. In the natural waters of the Jumilla vineyard area in Spain, diflufenican was detected at concentration of 530 ng L⁻¹ [36], which is five times higher than the concentration limit of 100 ng L⁻¹ established by European legislation. Similarly, in samples from the Dongjiang River in South China, the strobilurin group of fungicides, specifically dimoxystrobin, was found with a maximum concentration of 2.05 ng L⁻¹. A high concentration of the pesticide imazalil was determined in surface waters of the Júcar River in Spain with a concentration of 222.45 ng L⁻¹, as well as in wastewater from the agri-food industry with concentrations ranging

from 7038 to 19802 ng L⁻¹ [16]. In the Więcisa River in Poland, a high concentration of metconazole was detected at 5100 ng L⁻¹ [27], significantly exceeding the limit of 100 ng L⁻¹ set by European Union legislation for pesticide content in water [99]. Increased concentrations of prochloraz were reported in water systems of the Albufera natural park in Spain ranging from 2.1 to 3435 ng L⁻¹ [42]. The triazole organic compound tetraconazole was in groundwater in the Tidone Valley in northwestern Italy with concentrations ranging from 3 to 20 ng L⁻¹ [46]. Very low concentrations of pesticides were also found in seawater from the mouth of the Jiulong River in China, including ipconazole with concentrations ranging from n.d. to 0.966 ng L⁻¹ [7].

The processed data show that the highest number of occurrences of pharmaceutically active substances from the 4th WL was founded in surface waters. Antibiotics such as clindamycin [47], ofloxacin, sulfamethoxazole [25], and trimethoprim [58] were the priority group of pharmaceuticals. The presence of all antibiotics mentioned has mainly been described at different locations of surface water, but have also been found in wastewater [47,58], groundwater [47,58] and drinking water [47]. Found antibiotic concentrations in real water samples are different depending on matrix, but usually they are very low and often in the range of units to hundreds of ng L⁻¹, as in the case, for example, of clindamycin: 86 ng L⁻¹ for WWTP, 42 ng L⁻¹ for surface water, 1.2 ng L⁻¹ for groundwater and less than 0.1 ng L⁻¹ for drinking water [47]. The presence of antifungals at concentration levels of ng L⁻¹ such as clotrimazole 0.28–547.94 ng L⁻¹ [48], and miconazole n.d.–116.9 ng L⁻¹ [53] has also been confirmed in wastewater or fluconazole 7.5 ng L⁻¹ [49] in surface water.

An analysis of 21 WWTPs in 19 cities in Northeast China showed that the consumption of metformin, a widely used type 2 antidiabetic drug, is steadily increasing, but also depends on the economic situation of the population [28]. Metformin was detected in all wastewater samples with concentrations in the range of 2.42–53.6 mg L⁻¹. Another study has been performed on wastewater and drinking water samples by Kot-Wasik [14]. In this study, a significant difference was found between the concentration of metformin in wastewater (8101.4 ng L⁻¹) and drinking water (2.7 ng L⁻¹). In addition to the determination of metformin in wastewater [52], it is also important to determine its transformation product guanylurea [50,51], as it is not completely removed in the wastewater treatment and is continuously released into the aquatic environment. The European Union, the United States, Canada, Australia, and other countries do not have specific limits for metformin or guanylurea in water. Currently, no strict regulatory limits or maximum concentrations have been established for these substances in water.

The commonly utilized antidepressant venlafaxine [24,60] and its metabolically product O-desmethylvenlafaxine [54] have been found in different surface waters and wastewater in the concentration range of ng L⁻¹. Interestingly, the O-desmethylvenlafaxine as metabolite was found at higher concentrations than venlafaxine in a work of Coelho et al. [54]. For venlafaxine and its metabolites, there is no specific concentration limit in water established by European or global legislation.

UV filters, are mainly released into the aquatic environment at holiday destinations, so most research has focused on the determination of UV filters from the 4th WL in surface waters such as lakes and coastal bays [60], rivers [62,65], and in seawater samples [64], especially in tourist areas in the Mediterranean [13], or in the Canary Islands [64]. A minority of research on the occurrence of UV filters was found in wastewater [64] and drinking water [65]. Only, two organic UV filters, namely benzophenone-3 [61,62] and octocrylene [13,64,65], were investigated in all these studies. The weakly hydrophobic benzophenone-3 was found in surface water of Lake Villeneuve in France at around 3 ng L⁻¹ [61] and in two water source rivers at mean of concentrations of 1.2 or 11.2 ng L⁻¹ [62]. Hu et al. determined benzophenone-3 in surface water in the Pearl River in Guangzhou with concentrations up to 6 ng L⁻¹ and two WWTPs where the concentration of this UV filter varied by orders of magnitude depending on whether it

was wastewaters (90.5 and 54.8 ng L⁻¹) or effluent wastewaters (7.54 and 15.3 ng L⁻¹). Benzophenone-3 is listed among chemicals that are monitored, but specific limits for its concentration in water are not explicitly defined. Hydrophobic octocrylene was found in marine waters at three Mediterranean coastal sites located in the Gulf of Lion along the French Mediterranean coast impacted by diurnal recreational activities in summer, with different highest concentrations of 369, 102 and 59 ng L⁻¹ at three different sites studied [13]. Cadena-Aizaga et al. [64] focused not only on the determination of organic UV filters including octocrylene in seawater (171 mg L⁻¹) but also on its determination in wastewater from three WWTPs from Gran Canaria Island (Spain). In this study it was found that octocrylene represented the highest mass load in all the influent samples into the WWTPs (12 327 µg d⁻¹.1000 inhabitants⁻¹). Octocrylene was also the most frequently found UV filter in open-air swimming pools, aquaparks and seawater in summer in a study by Vila et al. [65] in Spain. For octocrylene, no specific concentration limits in water have been established by EU or global regulations.

4.2. Solid samples

Pesticides form a significant part of the 4th Watch list of substances and are most found in the environment in soil and sediment samples, mostly at low concentrations in ng g⁻¹. Given that there are several published papers, only a few values found for selected analytes will be presented.

Shen et al. determined metconazole in soil from China, with values up to 72 ng g⁻¹ and imazalil 3.3 ng g⁻¹ [66]. Calvo et al. determined prochloraz and tebuconazole from sediment samples of the aquatic systems of the Natural Park of the Albufera of Valencia (Spain) during the rice cultivation period, with values of 27.4 and 9 ng g⁻¹, respectively [42]. Zaidon et al. [43] focused their work on the whole group of azole compounds, they succeeded in determining several pesticides and fungicides with values of 0.44–34.81 ng g⁻¹, from rice fields demonstrating that the soil has a suppressive matrix with matrix effect values of 67–87 % for Watchlist compounds.

Pesticides of 4th WL have positive log K_{ow} values in the range of (roughly 1–6), indicating that they could also accumulate in living organisms. Several papers describe new methodologies for the determination of pesticides, fungicides, and herbicides [10,67] in biota, but their occurrence in real samples has not been determined, except for tebuconazole. Liu et al. [97] chose “zebrafish” as a typical model organism. The determined values of tebuconazole in the fish samples ranged from 0.33 to 3.67 mg kg⁻¹, an order of magnitude shift from the soil samples, but the differences in values are not evaluated in the paper itself for the inherent environmental risk. There is currently no scientific work available that monitors pesticides or herbicides in microplastics, or values are below the detection limits of analytical methodologies [18], but it is possible anticipate that this will change in the near future as microplastics and their properties are the subject of increased scientific interest.

The main source of pollution of soils and biota by pharmaceutical active compounds is through wastewaters from populated areas and near pharmaceutical factories. This has been amplified in the post-covid era, particularly by the widespread use of antidepressants. Venlafaxine, together with its degradation products (O-desmethyl venlafaxine), have been the most frequently detected in marine fish (fishponds and protected areas) at concentrations of 20.8 ng g⁻¹ [71]. Antibiotics and antifungals have been the most monitored in soils, where they could become overconcentrated. In the determination of antibiotics in soils, the concentrations determined were at very low levels e.g. trimethoprim n.d.-0.25 ng g⁻¹ [9], sulfmethoxazole n.d.-1 ng g⁻¹ [72].

Microplastics as a vector of contamination by polar organics is a relatively new phenomenon in the field of environmental protection. Several scientific works are available that also focus on “emerging” organics. For example, the determination of antibiotics in microplastics, found concentration ranges of n.d.-9.81 ng g⁻¹ for miconazole [18] and

90–101 ng g⁻¹ for trimethoprim [96]. It can also be seen from the research works that microplastics research is concentrated in the developed parts of the world and mainly in areas where tourism is the dominant source of income such as Hawaii, Macaronesia (this includes the Azores, Madeira, Canary Islands and Cape Verde Islands) and the Mediterranean region. It was quite interesting to find out that although there are several scientific works focusing on the development of analytical methods for the determination of guanylurea and metformin (active substances in antidiabetic drugs) [70,71], their real occurrence in soils, biota or microplastics is still poorly known, or they have not been determined in real samples.

Scientific research focusing on the determination and monitoring of UV filters also comes from areas where seaside tourism is dominant. Because of their non-polar properties and thus bioaccumulation capacity, several works have focused on their determination in fish liver or mussels (octocrylene 73–967 ng g⁻¹) [63], which are also a kind of indicator of the purity of the waters in which they are found. BP-3 is the most commonly determined with concentrations of n.d.-240 ng g⁻¹ [73] where the authors have determined bioaccumulation factors of 50 and 31.3–261.8 ng g⁻¹ for selected plants, respectively [63]. A few studies on this topic come from China and other countries of Asia, where the chemical and textile industries are close to rivers and may consequently be a potential source of pollution. In these studies, Benzophenone-3 has been determined most frequently in soils with concentrations ranging from n.d. to 70 ng g⁻¹ and 4.6–13.3 ng g⁻¹ [73]. In addition, avobenzene was also determined at levels of n.d.-75 ng g⁻¹ [61].

From the preceding sections, all groups of substances from the 4th WL are present in soils, biota as well as adsorbed on MPs surfaces. Their measured values are very low (ng g⁻¹ or less), but it would be interesting in the future to see more scientific works focusing on the risk assessment of bioaccumulation in living organisms.

5. Conclusions and future perspectives

The investigation about the presence of compounds from the latest 4th European Watch List (WL) across diverse environmental matrices, from literature published between 2000 and 2023, has revealed their widespread occurrence. These compounds, primarily of anthropogenic origin, are intricately linked to human consumption, chemical and pharmaceutical industry, as well as agricultural activities involving herbicides, insecticides, and fungicides. Collecting data on the presence of these substances in the environment is crucial to assess and evaluate whether they pose an ecological risk and, consequently, if they should be included in the list of priority substances to be identified.

Another significant concern is related to the presence of microplastics (MPs) in the environment and their ability to absorb organic contaminants from their surroundings. Studies have demonstrated that the coexistence of MPs and organic contaminants can intensify each other's toxicity, resulting in more pronounced adverse effects on the health and survival of living organisms.

This review provides a summary of the analytical methodologies used to determine these substances in various environmental matrices, including water, soil, biota, and microplastics. The evaluation of these methodologies offers a comprehensive overview of the available techniques for their determination. It offers a holistic view of the tools available for the identification and determination of these contaminants in different media, including MPs, which is crucial for environmental management and protection.

The different adsorption interaction mechanisms of pollutants on microplastics were discussed. This understanding is crucial for evaluating the transport and bioaccumulation of these substances in living organisms. Furthermore, the presence of substances from the WL was examined in various environmental matrices.

It is necessary to broaden the knowledge about environmental risks as well as the toxicity of compounds of the WL in the environment and living organisms. To achieve this, future research should focus on:

1. Establishing methodologies for the accurate detection of these compounds on different environmental matrices as well as adsorbed on MPs.
2. Understanding the adsorption/desorption mechanisms between MPs and pollutants adsorbed on them, as well as the effect of MPs weathering and degradation state on the adsorption of these chemical pollutants.
3. Examining the combined toxicity of MPs, along with other pollutants (such as pharmaceutical, personal care products and pesticides) on different environmental compartments.

These studies will contribute to a better understanding of the presence and effects of substances from the European Watch List, which in turn aid in the development of effective surveillance strategies to mitigate their impact on the environment and human health.

CRedit authorship contribution statement

Radoslav Halko: Writing – original draft, Investigation. **Sergio Santana-Viera:** Writing – original draft, Investigation. **Nicolas Milan Michalides:** Methodology, Investigation. **Zoraida Sosa-Ferrera:** Writing – review & editing. **José Juan Santana-Rodríguez:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Ludovit Schreiber:** Writing – original draft, Conceptualization.

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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Data availability

No data was used for the research described in the article.

References

- [1] Commission implementing decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council, Off. J. Eur. Union. <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32015D0495>, 2015 (accessed 25 April 2024).
- [2] L.Gomez Cortes, D. Marinov, I. Sanseverino, A. Navarro Cuenca, M. Niegowska, E. Porcel Rodriguez, F. Stefanelli, T. Lettieri, Selection of substances for the 4th watch list under the water framework directive, Off. J. Eur. Union (2022).
- [3] Commission implementing decision (EU) 2022/1307 of 22 July 2022 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council, Off. J. Eur. Union. <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32022D1307>, 2022 (accessed 25 April 2024).
- [4] S. Barreca, C. Forni, L. Colzani, L. Clerici, D. Daverio, P. Dellavedova, Study on the stability of antibiotics, pesticides and drugs in water by using a straightforward procedure applying hplc-mass spectrometric determination for analytical purposes, Separations 8 (2021) 179, <https://doi.org/10.3390/separations8100179>.
- [5] L. Shi, L. Chen, Y. Wan, H. Zeng, W. Xia, Spatial variation of fipronil and its derivatives in tap water and ground water from China and the fate of them during drinking water treatment in Wuhan, central China, Chemosphere 251 (2020) 126385, <https://doi.org/10.1016/j.chemosphere.2020.126385>.

- [6] B. Metin, A. Güleriyüz, D.S. Chormey, B.T. Zaman, S. Bakirdere, Determination of diflufenican and azaconazole pesticides in wastewater samples by GC-MS after preconcentration with stearic acid functionalized magnetic nanoparticles-based dispersive solid-phase extraction, *Environ. Monit. Assess.* 195 (2023) 32, <https://doi.org/10.1007/s10661-022-10699-0>.
- [7] Z. Liu, P. Qi, J. Wang, Z. Wang, S. Di, H. Xu, H. Zhao, Q. Wang, X. Wang, X. Wang, Development, validation, comparison, and implementation of a highly efficient and effective method using magnetic solid-phase extraction with hydrophilic-lipophilic-balanced materials for LC-MS/MS analysis of pesticides in seawater, *Sci. Total Environ.* 708 (2020) 135221, <https://doi.org/10.1016/j.scitotenv.2019.135221>.
- [8] X. Yao, F. Yang, W. Liu, S. Jin, Determination of four chiral pesticides in soil by QuEChERS-Ultra Performance Liquid Chromatography-Tandem Mass Spectrometry, *Wuhan. Univ. J. Nat. Sci.* 23 (2018) 369–375, <https://doi.org/10.1007/s11859-018-1336-8>.
- [9] A. Rashid, Y. Wang, Y. Li, C.P. Yu, Q. Sun, Simultaneous analysis of multiclass contaminants of emerging concern in sediments by liquid chromatography with tandem quadrupole mass spectrometry, *Environ. Toxicol. Chem.* 38 (2019) 1409–1422, <https://doi.org/10.1002/etc.4450>.
- [10] L. Han, Y. Sapozhnikova, Semi-automated high-throughput method for residual analysis of 302 pesticides and environmental contaminants in catfish by fast low-pressure GC-MS and UHPLC-MS/MS, *Food Chem.* 319 (2020) 126592, <https://doi.org/10.1016/j.foodchem.2020.126592>.
- [11] Y. Hao, Y. Sun, M. Li, X. Fang, Z. Wang, J. Zuo, C. Zhang, Adverse effects of polystyrene microplastics in the freshwater commercial fish, grass carp (*Ctenopharyngodon idella*): emphasis on physiological response and intestinal microbiome, *Sci. Total Environ.* 856 (2023) 159270, <https://doi.org/10.1016/j.scitotenv.2022.159270>.
- [12] S. Santana-Viera, S. Montesdeoca-Esponda, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, UV filters and UV stabilisers adsorbed in microplastic debris from beach sand, *Mar. Pollut. Bull.* 168 (2021) 112434, <https://doi.org/10.1016/j.marpolbul.2021.112434>.
- [13] M. Picot-Groz, H. Fenet, M.J. Martínez Bueno, D. Rosain, E. Gomez, Diurnal variations in personal care products in seawater and mussels at three Mediterranean coastal sites, *Environ. Sci. Pollut. Res.* 25 (2018) 9051–9059, <https://doi.org/10.1007/s11356-017-1100-1>.
- [14] A. Kot-Wasik, A. Jakimska, M. Śliwka-Kaszyńska, Occurrence and seasonal variations of 25 pharmaceutical residues in wastewater and drinking water treatment plants, *Environ. Monit. Assess.* 188 (2016) 661, <https://doi.org/10.1007/s10661-016-5637-0>.
- [15] J. Casado, D. Santillo, P. Johnston, Multi-residue analysis of pesticides in surface water by liquid chromatography quadrupole-Orbitrap high resolution tandem mass spectrometry, *Anal. Chim. Acta* 1024 (2018) 1–17, <https://doi.org/10.1016/j.aca.2018.04.026>.
- [16] M.C. Campos-Mañas, P. Plaza-Bolaños, A.B. Martínez-Piernas, J.A. Sánchez-Pérez, A. Agüera, Determination of pesticide levels in wastewater from an agro-food industry: target, suspect and transformation product analysis, *Chemosphere* 232 (2019) 152–163, <https://doi.org/10.1016/j.chemosphere.2019.05.147>.
- [17] L.M. Nejad, Y. Pashaei, B. Daraei, M. Forouzes, M. Shekarchi, Graphene oxide-based dispersive-solid phase extraction for preconcentration and determination of ampicillin sodium and clindamycin hydrochloride antibiotics in environmental water samples followed by HPLC-UV detection, *Iran. J. Pharm. Res.* 18 (2019) 642–657, <https://doi.org/10.22037/ijpr.2019.1100676>.
- [18] Y.W. Jia, Z. Huang, L.X. Hu, S. Liu, H.X. Li, J.L. Li, C.E. Chen, X.R. Xu, J.L. Zhao, G. G. Ying, Occurrence and mass loads of biocides in plastic debris from the Pearl River system, South China, *Chemosphere* 246 (2020) 125771, <https://doi.org/10.1016/j.chemosphere.2019.125771>.
- [19] J.M. Montiel-León, S.V. Duy, G. Muñoz, M. Amyot, S. Sauvé, Evaluation of on-line concentration coupled to liquid chromatography tandem mass spectrometry for the quantification of neonicotinoids and fipronil in surface water and tap water, *Anal. Bioanal. Chem.* 410 (2018) 2765–2779, <https://doi.org/10.1007/s00216-018-0957-2>.
- [20] N. Brucker, C. Menezes, M.F. Charão, L.C. Da Silva, T.S. Sant'Anna Oliveira, J. M. Menezes, I. Muller, A. Gioda, B.R.F. De Carvalho, O. De Castro Paz Calheiros, T. M. Rizzetti, R. Zanella, S.C. Garcia, Bioassays to screen the toxicity in drinking water samples collected in Brazilian rural area, *Toxicol. Res.* 10 (2021) 856–867, <https://doi.org/10.1093/toxres/tfab072>.
- [21] X. Guan, X. Zhu, B. Yu, T. Zhao, H. Zhang, Preparation of temperature sensitive molecularly imprinted polymer coatings on nickel foam for determination of ofloxacin in Yellow River water by solid-phase microextraction, *RSC Adv.* 5 (2015) 91716–91722, <https://doi.org/10.1039/c5ra15031k>.
- [22] R. He, J. Fan, Q. Tan, Y. Lai, X. Chen, T. Wang, Y. Jiang, Y. Zhang, W. Zhang, Enantioselective determination of metconazole in multi matrices by high-performance liquid chromatography, *Talanta* 178 (2018) 980–986, <https://doi.org/10.1016/j.talanta.2017.09.045>.
- [23] D. Ramírez-Morales, M. Masis-Mora, J.R. Montiel-Mora, J.C. Cambronero-Heinrichs, G. Pérez-Rojas, R. Tormo-Budowski, M. Méndez-Rivera, S. Briceño-Guevara, J.A. Gutiérrez-Quirós, V. Arias-Mora, L. Brenes-Alfaro, W. Beita-Sandí, C. E. Rodríguez-Rodríguez, Multi-residue analysis of pharmaceuticals in water samples by liquid chromatography- mass spectrometry: quality assessment and application to the risk assessment of urban-influenced surface waters in a metropolitan area of Central America, *Process Saf. Environ. Prot.* 153 (2021) 289–300, <https://doi.org/10.1016/j.psep.2021.07.025>.
- [24] D.L.D. Lima, C.P. Silva, M. Otero, Dispersive liquid-liquid microextraction for the quantification of venlafaxine in environmental waters, *J. Environ. Manag.* 217 (2018) 71–77, <https://doi.org/10.1016/j.jenvman.2018.03.060>.
- [25] L. Patrolecco, J. Rausedo, N. Ademollo, P. Grenni, M. Cardoni, C. Levantesi, M. L. Luprano, A.B. Caracciolo, Persistence of the antibiotic sulfamethoxazole in river water alone or in the co-presence of ciprofloxacin, *Sci. Total Environ.* 640–641 (2018) 1438–1446, <https://doi.org/10.1016/j.scitotenv.2018.06.025>.
- [26] A.L. de Toffoli, K. da Mata, M.C. Bisinoti, A.B. Moreira, Development, validation, and application of a method for the GC-MS analysis of fipronil and three of its degradation products in samples of water, soil, and sediment, *J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes* 50 (2015) 753–759, <https://doi.org/10.1080/03601234.2015.1058091>.
- [27] M. Tankiewicz, M. Biziuk, Fast, sensitive and reliable multi-residue method for routine determination of 34 pesticides from various chemical groups in water samples by using dispersive liquid-liquid microextraction coupled with gas chromatography-mass spectrometry, *Anal. Bioanal. Chem.* 410 (2018) 1533–1550, <https://doi.org/10.1007/s00216-017-0798-4>.
- [28] J.H. Yan, Y. Xiao, D.Q. Tan, X.T. Shao, Z. Wang, D.G. Wang, Wastewater analysis reveals spatial pattern in consumption of anti-diabetes drug metformin in China, *Chemosphere* 222 (2019) 688–695, <https://doi.org/10.1016/j.chemosphere.2019.01.151>.
- [29] M. Ghorbani, M. Chamsaz, G.H. Rounaghi, Glycine functionalized multiwall carbon nanotubes as a novel hollow fiber solid-phase microextraction sorbent for pre-concentration of venlafaxine and o-desmethylvenlafaxine in biological and water samples prior to determination by high-performance liquid chromatography, *Anal. Bioanal. Chem.* 408 (2016) 4247–4256, <https://doi.org/10.1007/s00216-016-9518-8>.
- [30] H.I. Mokhtar, R.A. Abdel-Salam, G.M. Hadad, Tolerance intervals modeling for design space of a salt assisted liquid-liquid microextraction of trimethoprim and six common sulfonamide antibiotics in environmental water samples, *J. Chromatogr. A* 1586 (2019) 18–29, <https://doi.org/10.1016/j.chroma.2018.12.003>.
- [31] X. Li, B. Li, M. Chen, M. Yan, X. Cao, J. Yin, Z. Zhang, Preparation of magnetic zeolitic imidazolate framework-8 for magnetic solid-phase extraction of strobilurin fungicides from environmental water samples, *Anal. Methods* 13 (2021) 2943–2950, <https://doi.org/10.1039/d1ay00645b>.
- [32] S. Wu, T. Jin, J. Cheng, H. Zhou, M. Cheng, Air-assisted liquid liquid-microextraction for the analysis of fungicides from environmental water and juice samples, *J. Chromatogr. Sci.* 53 (2015) 1007–1012, <https://doi.org/10.1093/chromsci/bmu136>.
- [33] M.B. Medina, M.S. Munitz, S.L. Resnik, Validation and expanded uncertainty determination of pesticides in water; and their survey on paddy rice irrigation water from Argentina, *J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes* 55 (2020) 983–989, <https://doi.org/10.1080/03601234.2020.1807262>.
- [34] S. Corcoran, C.D. Metcalfe, T. Sultana, M.V. Amé, M.L. Menone, Pesticides in surface waters in argentina monitored using polar organic chemical integrative samplers, *Bull. Environ. Contam. Toxicol.* 104 (2020) 21–26, <https://doi.org/10.1007/s00128-019-02758-z>.
- [35] M. Yang, X. Wu, Y. Jia, X. Xi, X. Yang, R. Lu, S. Zhang, H. Gao, W. Zhou, Use of magnetic effervescent tablet-assisted ionic liquid dispersive liquid-liquid microextraction to extract fungicides from environmental waters with the aid of experimental design methodology, *Anal. Chim. Acta* 906 (2016) 118–127, <https://doi.org/10.1016/j.aca.2015.12.019>.
- [36] E. Herrero-Hernández, A.B. Simón-Egea, M.J. Sánchez-Martín, M.S. Rodríguez-Cruz, M.S. Andrades, Monitoring and environmental risk assessment of pesticide residues and some of their degradation products in natural waters of the Spanish vineyard region included in the Denomination of Origin Jumilla, *Environ. Pollut.* 264 (2020) 114666, <https://doi.org/10.1016/j.envpol.2020.114666>.
- [37] M. Amde, Z.Q. Tan, R. Liu, J.F. Liu, Nanofluid of zinc oxide nanoparticles in ionic liquid for single drop liquid microextraction of fungicides in environmental waters prior to high performance liquid chromatographic analysis, *J. Chromatogr. A* 1395 (2015) 7–15, <https://doi.org/10.1016/j.chroma.2015.03.049>.
- [38] Y. Wan, T.M. Tran, V.T. Nguyen, A. Wang, J. Wang, K. Kannan, Neonicotinoids, fipronil, chlorpyrifos, carbendazim, chlorotriazines, chlorophenoxy herbicides, bentazon, and selected pesticide transformation products in surface water and drinking water from northern Vietnam, *Sci. Total Environ.* 750 (2021) 141507, <https://doi.org/10.1016/j.scitotenv.2020.141507>.
- [39] S.D. Supowit, A.M. Sadaria, E.J. Reyes, R.U. Halden, Mass balance of fipronil and total toxicity of fipronil-related compounds in process streams during conventional wastewater and wetland treatment, *Environ. Sci. Technol.* 50 (2016) 1519–1526, <https://doi.org/10.1021/acs.est.5b04516>.
- [40] L. Kharbouche, M.D. Gil García, A. Lozano, H. Hamaizi, M.M. Galera, Solid phase extraction of pesticides from environmental waters using an MSU-1 mesoporous material and determination by UPLC-MS/MS, *Talanta* 199 (2019) 612–619, <https://doi.org/10.1016/j.talanta.2019.02.092>.
- [41] A.E. Bulgurcuoğlu, B.Y. Durak, D.S. Chormey, S. Bakirdere, Development of a switchable solvent liquid phase extraction method for the determination of chlorthiamid, ethyl parathion, penconazole and fludioxonil pesticides in well, tap and lake water samples by gas chromatography mass spectrometry, *Microchem. J.* 168 (2021) 106381, <https://doi.org/10.1016/j.microc.2021.106381>.
- [42] S. Calvo, S. Romo, J. Soria, Y. Picó, Pesticide contamination in water and sediment of the aquatic systems of the Natural Park of the Albufera de Valencia (Spain) during the rice cultivation period, *Sci. Total Environ.* 774 (2021) 145009, <https://doi.org/10.1016/j.scitotenv.2021.145009>.
- [43] S.Z. Zaidon, Y.B. Ho, H. Hamsan, Z. Hashim, N. Saari, S.M. Praveena, Improved QuEChERS and solid phase extraction for multi-residue analysis of pesticides in paddy soil and water using ultra-high performance liquid chromatography tandem mass spectrometry, *Microchem. J.* 145 (2019) 614–621, <https://doi.org/10.1016/j.microc.2018.11.025>.

- [44] L. Jia, J. Yang, W. Zhao, X. Jing, Air-assisted ionic liquid dispersive liquid-liquid microextraction based on solidification of the aqueous phase for the determination of triazole fungicides in water samples by high-performance liquid chromatography, *RSC Adv.* 9 (2019) 36664–36669, <https://doi.org/10.1039/c9ra07348e>.
- [45] N. Liu, F. Dong, J. Xu, X. Liu, Z. Chen, Y. Tao, X. Pan, X. Chen, Y. Zheng, Stereoselective determination of tebuconazole in water and zebrafish by supercritical fluid chromatography tandem mass spectrometry, *J. Agric. Food Chem.* 63 (2015) 6297–6303, <https://doi.org/10.1021/acs.jafc.5b02450>.
- [46] R. Zambito Marsala, E. Capri, E. Russo, M. Bisagni, R. Colla, L. Lucini, A. Gallo, N. A. Suci, First evaluation of pesticides occurrence in groundwater of Tidone Valley, an area with intensive viticulture, *Sci. Total Environ.* 736 (2020) 139730, <https://doi.org/10.1016/j.scitotenv.2020.139730>.
- [47] L. Boulard, G. Dierkes, T. Ternes, Utilization of large volume zwitterionic hydrophilic interaction liquid chromatography for the analysis of polar pharmaceuticals in aqueous environmental samples: benefits and limitations, *J. Chromatogr. A* 1535 (2018) 27–43, <https://doi.org/10.1016/j.chroma.2017.12.023>.
- [48] Y. Yang, Y. Ji, Y. Gao, Z. Lin, Y. Lin, Y. Lu, L. Zhang, Antibiotics and antimicrobials in waste water treatment plants: concentrations, removal efficiency, spatial and temporal variations, prediction, and ecological risk assessment, *Environ. Res.* 215 (2022) 114135, <https://doi.org/10.1016/j.envres.2022.114135>.
- [49] C.L. Chitescu, G. Kaklamanos, A.I. Nicolau, A.A.M.L. Stolker, High sensitive multiresidue analysis of pharmaceuticals and antifungals in surface water using U-HPLC-Q-Exactive Orbitrap HRMS. Application to the Danube river basin on the Romanian territory, *Sci. Total Environ.* 532 (2015) 501–511, <https://doi.org/10.1016/j.scitotenv.2015.06.010>.
- [50] S. Tisler, C. Zwiener, Formation and occurrence of transformation products of metformin in wastewater and surface water, *Sci. Total Environ.* 628–629 (2018) 1121–1129, <https://doi.org/10.1016/j.scitotenv.2018.02.105>.
- [51] C.I. Kosma, D.A. Lambropoulou, T.A. Albanis, Comprehensive study of the antidiabetic drug metformin and its transformation product guanlylurea in Greek wastewaters, *Water Res.* 70 (2015) 436–448, <https://doi.org/10.1016/j.watres.2014.12.010>.
- [52] Y. Xing, Y. Yu, Y. Men, Emerging investigators series: occurrence and fate of emerging organic contaminants in wastewater treatment plants with an enhanced nitrification step, *Environ. Sci. Water Res. Technol.* 4 (2018) 1412–1426, <https://doi.org/10.1039/c8ew00278a>.
- [53] A.L.C. de Barros, F.F. Schmidt, S.F. de Aquino, R.J.C.F. Afonso, Determination of nine pharmaceutical active compounds in surface waters from Paraopeba River Basin in Brazil by LTPE-HPLC-ESI-MS/MS, *Environ. Sci. Pollut. Res.* 25 (2018) 19962–19974, <https://doi.org/10.1007/s11356-018-2123-y>.
- [54] M.M. Coelho, A.R. Lado Ribeiro, J.C.G. Sousa, C. Ribeiro, C. Fernandes, A.M. T. Silva, M.E. Tiritan, Dual enantioselective LC-MS/MS method to analyse chiral drugs in surface water: monitoring in Douro River estuary, *J. Pharm. Biomed. Anal.* 170 (2019) 89–101, <https://doi.org/10.1016/j.jpba.2019.03.032>.
- [55] H. Wu, Y. Shi, X. Guo, S. Zhao, J. Du, H. Jia, L. He, L. Du, Determination and removal of sulfonamides and quinolones from environmental water samples using magnetic adsorbents, *J. Sep. Sci.* 39 (2016) 4398–4407, <https://doi.org/10.1002/jssc.2016006631>.
- [56] P. Grenni, L. Patrolocco, J. Rauseo, F. Spataro, M. Di Lenola, G. Aimola, M. Zacchini, F. Pietrini, D. Di Baccio, I.C. Stanton, W.H. Gaze, A. Barra Caracciolo, Sulfamethoxazole persistence in a river water ecosystem and its effects on the natural microbial community and Lemna minor plant, *Microchem. J.* 149 (2019) 103999, <https://doi.org/10.1016/j.microc.2019.103999>.
- [57] F. Mehrabi, M. Mohamadi, A. Mostafavi, H. Hakimi, T. Shamspur, Magnetic solid phase extraction based on PVA-TEOS / grafted Fe₃O₄@SiO₂ magnetic nanofibers for analysis of sulfamethoxazole and trimethoprim in water samples, *J. Solid State Chem.* 292 (2020) 121716, <https://doi.org/10.1016/j.jssc.2020.121716>.
- [58] C. Kim, H.D. Ryu, E.G. Chung, Y. Kim, Determination of 18 veterinary antibiotics in environmental water using high-performance liquid chromatography-q-orbitrap combined with on-line solid-phase extraction, *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 1084 (2018) 158–165, <https://doi.org/10.1016/j.jchromb.2018.03.038>.
- [59] S. Khulu, S. Ncube, T. Kgame, E. Mavhunga, L. Chimuka, Synthesis, characterization and application of a molecularly imprinted polymer as an adsorbent for solid-phase extraction of selected pharmaceuticals from water samples, *Polym. Bull.* 79 (2022) 1287–1307, <https://doi.org/10.1007/s00289-021-03553-9>.
- [60] L.D. Ma, J. Li, J.J. Li, M. Liu, D.Z. Yan, W.Y. Shi, G. Xu, Occurrence and source analysis of selected antidepressants and their metabolites in municipal wastewater and receiving surface water, *Environ. Sci. Process. Impacts* 20 (2018) 1020–1029, <https://doi.org/10.1039/c8em00077h>.
- [61] S.K. Fagervoid, A.S. Rodrigues, C. Rohée, R. Roe, M. Bourrain, D. Stien, P. Lebaron, Occurrence and environmental distribution of 5 UV filters during the summer season in different water bodies, *Water Air Soil Pollut.* 230 (2019) 172, <https://doi.org/10.1007/s11270-019-4217-7>.
- [62] L.X. Hu, Y.X. Cheng, D. Wu, L. Fan, J.H. Zhao, Q. Xiong, Q.L. Chen, Y.S. Liu, G. G. Ying, Continuous input of organic ultraviolet filters and benzothiazoles threatens the surface water and sediment of two major rivers in the Pearl River Basin, *Sci. Total Environ.* 798 (2021) 149299, <https://doi.org/10.1016/j.scitotenv.2021.149299>.
- [63] C.L. Mitchellmore, K. He, M. Gonsior, E. Hain, A. Heyes, C. Clark, R. Younger, P. Schmitt-Kopplin, A. Feerick, A. Conway, L. Blaney, Occurrence and distribution of UV-filters and other anthropogenic contaminants in coastal surface water, sediment, and coral tissue from Hawaii, *Sci. Total Environ.* 670 (2019) 398–410, <https://doi.org/10.1016/j.scitotenv.2019.03.034>.
- [64] M.I. Cadena-Aizaga, S. Montesdeoca-Esponda, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria Island (Canary Islands, Spain), *Environ. Pollut.* 300 (2022) 118843, <https://doi.org/10.1016/j.envpol.2022.118843>.
- [65] M. Vila, J. Pablo Lamas, C. Garcia-Jares, T. Dagnac, M. Llompard, Ultrasound-assisted emulsification microextraction followed by gas chromatography-mass spectrometry and gas chromatography-tandem mass spectrometry for the analysis of UV filters in water, *Microchem. J.* 124 (2016) 530–539, <https://doi.org/10.1016/j.microc.2015.09.023>.
- [66] Y. Shen, X. Yao, S. Jin, F. Yang, Enantiomer/stereoisomer-specific residues of metalaxyl, napropamide, triticonazole, and metconazole in agricultural soils across China, *Environ. Monit. Assess.* 193 (2021) 773, <https://doi.org/10.1007/s10661-021-09562-5>.
- [67] G.P. Black, E.E. Woodward, C.J. Sanders, M.S. Gross, M.L. Hladik, Multiresidue extraction of current-use pesticides from complex solid matrices using energized dispersive guided extraction with analysis by gas and liquid chromatography tandem mass spectroscopy, *Chemosphere* 327 (2023) 138550, <https://doi.org/10.1016/j.chemosphere.2023.138550>.
- [68] M. Biel-Maeso, C. Corada-Fernández, P.A. Lara-Martín, Determining the distribution of pharmaceutically active compounds (PhACs) in soils and sediments by pressurized hot water extraction (PHWE), *Chemosphere* 185 (2017) 1001–1010, <https://doi.org/10.1016/j.chemosphere.2017.07.094>.
- [69] Y. Zhong, Z.F. Chen, S.S. Liu, X. Dai, X. Zhu, G. Zhong, S. Liu, G. Liu, Z. Cai, Analysis of azole fungicides in fish muscle tissues: Multi-factor optimization and application to environmental samples, *J. Hazard. Mater.* 324 (2017) 535–543, <https://doi.org/10.1016/j.jhazmat.2016.11.024>.
- [70] S. Knoll, S. Jacob, S. Mieck, R. Triebkorn, T. Braunbeck, C. Huhn, Development of a capillary electrophoresis–mass spectrometry method for the analysis of metformin and its transformation product guanlylurea in biota, *Anal. Bioanal. Chem.* 412 (2020) 4985–4996, <https://doi.org/10.1007/s00216-020-02759-6>.
- [71] D.P. Manjarrés, N. Montemurro, S. Pérez, Development of a USE/d-SPE and targeted DIA-Orbitrap-MS acquisition methodology for the analysis of wastewater-derived organic pollutants in fish tissues and body fluids, *MethodsX* 9 (2022) 101705, <https://doi.org/10.1016/j.mex.2022.101705>.
- [72] T.F.T. Omar, A.Z. Aris, F.M. Yusoff, Multiclass analysis of emerging organic contaminants in tropical marine biota using improved QuEChERS extraction followed by LC MS/MS, *Microchem. J.* 164 (2021) 106063, <https://doi.org/10.1016/j.microc.2021.106063>.
- [73] Y. Lyu, G.H. Li, Y. He, Y.H. Li, Z.W. Tang, Occurrence and distribution of organic ultraviolet absorbents in soils and plants from a typical industrial area in South China, *Sci. Total Environ.* 846 (2022) 157383, <https://doi.org/10.1016/j.scitotenv.2022.157383>.
- [74] Z. Gao, Y. Wu, H. Zhao, F. Ji, Q. He, S. Li, Concentration determination of new fungicide in river water by ultrasound-assisted emulsification micro-extraction and reversed-phase high performance liquid chromatography, *Anal. Methods* 4 (2012) 2365–2368, <https://doi.org/10.1039/c2ay25372k>.
- [75] K. Kotnik, T. Kosjek, U. Krajnc, E. Heath, Trace analysis of benzophenone-derived compounds in surface waters and sediments using solid-phase extraction and microwave-Assisted extraction followed by gas chromatography-mass spectrometry, *Anal. Bioanal. Chem.* 406 (2014) 3179–3190, <https://doi.org/10.1007/s00216-014-7749-0>.
- [76] K. Ugwu, A. Herrera, M. Gómez, Microplastics in marine biota: a review, *Mar. Pollut. Bull.* 169 (2021) 112540, <https://doi.org/10.1016/j.marpolbul.2021.112540>.
- [77] Y. Xia, S. Niu, J. Yu, Microplastics as vectors of organic pollutants in aquatic environment: a review on mechanisms, numerical models, and influencing factors, *Sci. Total Environ.* 887 (2023) 164008, <https://doi.org/10.1016/j.scitotenv.2023.164008>.
- [78] J. Martín, J.L. Santos, I. Aparicio, E. Alonso, Microplastics and associated emerging contaminants in the environment: analysis, sorption mechanisms and effects of co-exposure, *Trends Environ. Anal. Chem.* 35 (2022) e00170, <https://doi.org/10.1016/j.teac.2022.e00170>.
- [79] Y. Vieira, E.C. Lima, E.L. Foletto, G.L. Dotto, Microplastics physicochemical properties, specific adsorption modeling and their interaction with pharmaceuticals and other emerging contaminants, *Sci. Total Environ.* 753 (2021) 141981, <https://doi.org/10.1016/j.scitotenv.2020.141981>.
- [80] L. Fu, J. Li, G. Wang, Y. Luan, W. Dai, Adsorption behavior of organic pollutants on microplastics, *Ecotoxicol. Environ. Saf.* 217 (2021) 112207, <https://doi.org/10.1016/j.ecoenv.2021.112207>.
- [81] F. Wang, K.M. Shih, X.Y. Li, The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics, *Chemosphere* 119 (2015) 841–847, <https://doi.org/10.1016/j.chemosphere.2014.08.047>.
- [82] A. Elizalde-Velázquez, S. Subbiah, T.A. Anderson, M.J. Green, X. Zhao, J.E. Cañas-Carrell, Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics, *Sci. Total Environ.* 715 (2020) 136974, <https://doi.org/10.1016/j.scitotenv.2020.136974>.
- [83] T. Atugoda, M. Vithanage, H. Wijesekara, N. Bolan, A.K. Sarmah, M.S. Bank, S. You, Y.S. Ok, Interactions between microplastics, pharmaceuticals and personal care products: implications for vector transport, *Environ. Int.* 149 (2021) 106367, <https://doi.org/10.1016/j.envint.2020.106367>.
- [84] J.P. Rodrigues, A.C. Duarte, J. Santos-Echeandía, T. Rocha-Santos, Significance of interactions between microplastics and POPs in the marine environment: A critical overview, *TrAC Trends Anal. Chem.* 111 (2019) 252–260, <https://doi.org/10.1016/j.trac.2018.11.038>.

- [85] C. Wu, K. Zhang, X. Huang, J. Liu, Sorption of pharmaceuticals and personal care products to polyethylene debris, *Environ. Sci. Pollut. Res.* 23 (2016) 8819–8826, <https://doi.org/10.1007/s11356-016-6121-7>.
- [86] I.A. O'Connor, L. Golsteijn, A.J. Hendriks, Review of the partitioning of chemicals into different plastics: consequences for the risk assessment of marine plastic debris, *Mar. Pollut. Bull.* 113 (2016) 17–24, <https://doi.org/10.1016/j.marpolbul.2016.07.021>.
- [87] O.H. Fred-Ahmadu, G. Bhagwat, I. Oluyoye, N.U. Benson, O.O. Ayejuyo, T. Palanisami, Interaction of chemical contaminants with microplastics: principles and perspectives, *Sci. Total Environ.* 706 (2020) 135978, <https://doi.org/10.1016/j.scitotenv.2019.135978>.
- [88] N. Liu, F. Yu, Y. Wang, J. Ma, Effects of environmental aging on the adsorption behavior of antibiotics from aqueous solutions in microplastic-graphene coexisting systems, *Sci. Total Environ.* 806 (2022) 150956, <https://doi.org/10.1016/j.scitotenv.2021.150956>.
- [89] W. Gong, M. Jiang, P. Han, G. Liang, T. Zhang, G. Liu, Comparative analysis on the sorption kinetics and isotherms of fipronil on nondegradable and biodegradable microplastics, *Environ. Pollut.* 254 (2019) 112927, <https://doi.org/10.1016/j.envpol.2019.07.095>.
- [90] G. Liu, Z. Zhu, Y. Yang, Y. Sun, F. Yu, J. Ma, Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater 246 (2019) 26–33, <https://doi.org/10.1016/j.envpol.2018.11.100>.
- [91] T. Wan, S. Lu, W. Cheng, J. Ren, M. Wang, B. Hu, Z. Jia, Y. Li, Y. Sun, A spectroscopic and theoretical investigation of interaction mechanisms of tetracycline and polystyrene nanospheres under different conditions, *Environ. Pollut.* 249 (2019) 398–405, <https://doi.org/10.1016/j.envpol.2019.03.049>.
- [92] M. Llorca, G. Schirinzi, M. Martínez, D. Barceló, M. Farré, Adsorption of perfluoroalkyl substances on microplastics under environmental conditions, *Environ. Pollut.* 235 (2018) 680–691, <https://doi.org/10.1016/j.envpol.2017.12.075>.
- [93] L. Ding, R. Mao, S. Ma, X. Guo, L. Zhu, High temperature depended on the ageing mechanism of microplastics under different environmental conditions and its effect on the distribution of organic pollutants, *Water Res.* 174 (2020) 115634, <https://doi.org/10.1016/j.watres.2020.115634>.
- [94] Y. Li, M. Li, Z. Li, L. Yang, X. Liu, Effects of particle size and solution chemistry on Triclosan sorption on polystyrene microplastic, *Chemosphere* 231 (2019) 308–314, <https://doi.org/10.1016/j.chemosphere.2019.05.116>.
- [95] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Sep. Purif. Methods* 29 (2000) 189–232, <https://doi.org/10.1081/SPM-100100009>.
- [96] A. Abdurahman, K. Cui, J. Wu, S. Li, R. Gao, J. Dai, W. Liang, F. Zeng, Adsorption of dissolved organic matter (DOM) on polystyrene microplastics in aquatic environments: kinetic, isotherm and site energy distribution analysis, *Ecotoxicol. Environ. Saf.* 198 (2020) 110658, <https://doi.org/10.1016/j.ecoenv.2020.110658>.
- [97] Z. Liu, Q. Qin, Z. Hu, L. Yan, U.I. leong, Y. Xu, Adsorption of chlorophenols on polyethylene terephthalate microplastics from aqueous environments: kinetics, mechanisms and influencing factors, *Environ. Pollut.* 265 (2020) 114926, <https://doi.org/10.1016/j.envpol.2020.114926>.
- [98] C.E. Smit, *Water quality standards for imidacloprid: Proposal for an update according to the Water Framework Directive*, National Institute for Public Health and the Environment, Bilthoven, The Netherlands, 2014.
- [99] DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, *Off. J. Eur. Union*. <https://eur-lex.europa.eu/%20LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:EN:PDF>, 2013 (accessed 25 April 2024).