Microchemical Journal 207 (2024) 111987

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Enhancing the determination of European Union Watch List Organic pollutants adsorbed on microplastic debris by single-step ultrasound-assisted extraction coupled with ultra-high performance liquid chromatography tandem mass spectrometry

Ludovit Schreiber [a,*], Nicolas Milan Michalides [b], Zoraida Sosa-Ferrera [a,*], José Juan Santana-Rodríguez [a]

[a] Instituto Universitario de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain
[b] Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, 842 15 Bratislava, Slovakia

ARTICLE INFO

Keywords:
European Union Watch List Organic pollutants
Microplastics
Beaches
Ultrasound-assisted extraction
Ultra-high performance liquid chromatography
Mass spectrometry

ABSTRACT

Microplastics (MPs) have become a concerning environmental issue for their ubiquity and potential to adsorb organic pollutants, and for posing risks for ecosystems and human health. This study presents an effective optimised method to determine the variability of the concentrations of 25 emerging organic pollutants from the latest EU Watch List adsorbed on MP debris. The method involves a single-step ultrasound-assisted extraction (UAE), followed by ultrahigh-performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS), for their determination, which results in enhanced efficiency and precision in pollutants identification.

By this approach, the linearity for all the analysed compounds exhibited correlation coefficients (r^2) over 0.990, with limits of detection (LOD) and limits of quantification (LOQ) ranging from 0.03 to 8.55 ng/g and 0.07 to 28.50 ng/g, respectively. The mean recovery of 71–106 % was achieved and relative standard deviations (RSDs) were less than 15 %.

Subsequently, the method was applied to screen for the target analytes in the MPs debris samples collected from many sandy beaches on the Tenerife Island (Canary Islands, Spain). The results indicated the presence of the selected micropollutants at concentrations ranging from 15 to 824 ng/g, with the highest concentrations for UV filter octocrylene, which was present in 83.3 % of the analysed samples.

The proposed method offers a streamlined environment-friendly approach for adsorbed pollutants extraction from stranded MP debris, which emphasises its significance as a potential source of pollution in various environments.

1. Introduction

Recently, significant concern been voiced about the widespread accumulation of plastics and microplastics (MPs) in oceans [1,2], as well as their ingestion by marine organisms [3,4]. MPs can originate from the degradation of larger plastic objects or can be intentionally manufactured as pellets for use in the plastic industry [5]. Additionally, treated sewage discharge has been identified as a significant source of MPs pollution [6,7].

The impact of MPs on the environment extends beyond physical effects, and includes chemical consequences that result from their ability to adsorb and accumulate both persistent and non-persistent organic pollutants [8,9]. Therefore, MPs have been identified as significant transport vectors for pollutants in natural water environments and the food web [10–12]. To safeguard the health of aquatic ecosystems and to preserve the well-being of both the marine life and human populations that depend on these environments, it is necessary to prevent pollution from organic pollutants in general, and also from MPs, to avoid their interaction [13].

The European Union (EU) has implemented the EU Water Framework Directive (WFD) to reduce pollution and to protect Europe's environment and human health [14]. As part of the WFD, the EU

* Corresponding authors.
E-mail addresses: ludovit.schreiber@ulpgc.es (L. Schreiber), zoraida.sosa@ulpgc.es (Z. Sosa-Ferrera).

https://doi.org/10.1016/j.microc.2024.111987
Received 16 September 2024; Received in revised form 18 October 2024; Accepted 19 October 2024
Available online 20 October 2024

introduced the first Watch List of substances (Decision 2015/495) [15]. The purpose of the Watch List is to collect monitoring data about these substances throughout the EU. These substances are selected based on the potential significant risks that they may pose for the aquatic environment. The Watch List was last updated in 2022 (Decision 2022/1307) according to Directive 2008/105/EC [16]. The substances on the Watch List can be categorised based on their chemical structure and functional application into three groups: a) industrial products used to produce materials or as process agents; b) plant protection products and biocides; c) pharmaceuticals and illicit drugs [17,18].

However, due to insufficient monitoring data, conclusive assessments of actual risks are not yet possible. Therefore, it is crucial to identify, monitor, and quantify these substances to better understand their potential impact on the environment.

An important concern associated with environmental pollution is the presence of mixtures of multiple components that can enhance the toxic effects of these compounds. Additionally, the presence of MPs, which may coexist in the environment with these emerging contaminants, aggravates the problem. The ingestion of contaminated MPs by organism can also increase the desorption of pollutants, amplifying their bioavailability and toxicity. This interaction between MPs and these contaminants represents an additional challenge in environmental pollution management and underscores the importance of addressing these issues comprehensively and in coordinate manner [19,20]. The methodology to determine all these substances adsorbed on MPs is currently lacking [21–24]. Several authors and research teams investigate the organic substances adsorbed on MPs, but published works tend to focus on specific groups of substances, such as persistent organic pollutants, UV filters, hormones, among others [25–30].

The aim of this proposal is to explore an alternative and environment-friendly extraction method [31] for all the pollutants on the latest Watch List that are adsorbed on MPs. This method is based on single-step ultrasonic-assisted extraction (UAE) instead of traditional extraction methods like soaking or maceration. Traditional methods often involve large solvent volumes and lengthy extraction times, which render them less suitable for routine use.

In this study, an UAE method, followed by an ultrahigh-performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS) analysis, was optimised and developed. This efficient approach was then applied to analyse the target compounds adsorbed on the fragment and pellet samples obtained in several beach sands on the Tenerife Island (Canary Islands, Spain).

2. Experimental

2.1. Materials and reagents

Twenty-five target compounds (Table 1) were acquired from Sigma-Aldrich (Massachusetts, USA). To prepare stock solutions for individual analytes, the target compounds were dissolved in methanol to a concentration of 200 ng/mL and stored in glass-stoppered bottles at −20 °C in the dark until further use. Subsequently, an intermediate standard

Table 1
Selected compounds and MS/MS acquisition parameters.

Name of substance/group of substances	Formula	Monoisotopic mass	MRM Transition	Collision energy (V)	Cone voltage (V)	Retention time (min)
Antibiotics Group 1						
Sulfamethoxazole	C10H11N3O3S	253.0	254.2 > 108.0, 92.1	26	22	4.31
Trimethoprim	C14H18N4O3	290.1	291.3 > 230.0, 123.0	48	26	3.50
Antidepressants						
Venlafaxine	C17H27NO2	277.2	278.4 > 260.3, 58.0	26	18	4.15
O-desmethylvenlafaxine	C16H25NO2	263.2	264.4 > 246.4, 58.0	28	18	3.68
Azole Compounds (antifungals)						
Clotrimazole	C22H17ClN2	344.1	277.3 > 241.2, 165.1	36	22	5.69
Fluconazole	C13H12F2N6O	306.1	307.3 > 238.1, 220.1	30	18	4.02
Imazalil	C14H14Cl2N2O	296.0	297.2 > 159.0, 69.0	36	24	4.80
Ipconazole	C18H24ClN3O	333.2	334.3 > 70.0, 125.0	32	24	6.50
Metconazole	C17H22ClN3O	319.1	320.3 > 70.0, 125.0	34	20	6.21
Miconazole	C18H14Cl4N2O	414.0	415.2 > 159.0, 69.0	50	30	5.85
Penconazole	C13H15Cl2N3	283.1	284.3 > 70.0, 159.0	28	14	6.17
Prochloraz	C15H16Cl3N3O2	375.0	376.2 > 308.0, 70.0	20	10	6.32
Tebuconazole	C16H22ClN3O	307.1	308.3 > 70.0, 125.0	32	20	6.07
Tetraconazole	C13H11Cl2F4N3O	371.0	372.2 > 159.0, 70.0	38	24	6.03
Fungicides & Pesticides & Herbicides						
Dimoxystrobin	C19H22N2O3	326.2	327.4 > 205.1, 116.0	18	8	6.27
Azoxystrobin	C22H17N3O5	403.1	404.3 > 372.1, 344.2	26	12	5.98
Famoxadone	C22H18N2O4	374.1	392.4 > 331.2, 238.1	18	6	6.54
Diflufenican	C19H11F5N2O2	394.1	395.3 > 266.0, 246.1	42	24	6.73
Fipronil	C12H4Cl2F6N4OS	436.0	437.2 > 368.0, 290.1	40	14	6.39
Antibiotics Group 2						
Clindamycin	C18H33ClN2O5S	424.2	425.4 > 377.3, 126.1	20	38	4.22
Ofloxacin	C18H20FN3O4	361.1	362.4 > 318.2, 261.2	38	18	3.62
Antidiabetic drugs						
Metformin	C4H11N5	129.1	130.2 > 71.0, 60.0	24	12	0.75
Guanylurea	C2H6N4O	102.1	103.2 > 71.0, 60.0	20	10	0.7
Sunscreen agents						
Avobenzone	C20H22O3	310.2	311.2 > 161.1, 135.1	20	20	7.59
Octocrylene	C24H27NO2	361.2	362.4, 379.5 > 250.0	28	12	7.65

solution containing a mixture of all the analytes (concentration of each analyte was 400 ng/mL), was prepared by further dissolution in methanol and stored at −20 °C in the dark. These intermediate standard solutions were prepared daily. The LC-MS grade methanol, acetonitrile and water employed for the mobile phase and extraction procedures were purchased from VWR (Pennsylvania, USA). The ammonium formate and formic acid utilised for buffering the mobile phase were purchased from Panreac Química (Barcelona, Spain). Their purities were over 99 %. The water-containing solutions were prepared daily. Polypropylene commercial pellets with nominal size of 4 mm were obtained from Sigma-Aldrich (Madrid, Spain).

2.2. Instrumentation

In order to extract the target analytes from MPs, an ultrasonic bath manufactured by VWR (Pennsylvania, USA) was employed. The ultrasonic bath operated at a frequency of 45 kHz, which performed effective and efficient extractions of the analytes from MPs.

Following extraction, a UHPLC-MS/MS system was employed for the separation and detection of analytes. This system consists of a quaternary pump, a sample manager capable of injecting up to 96 samples, a column oven and a triple quadrupole detector with an electrospray interface (ESI). The UPLC system was controlled and the results were obtained using the MassLynx Mass Spectrometry software. They were all supplied by Waters Waters Chromatography, Barcelona, Spain

2.3. Sample collection

Samples were collected from several beaches located on the Tenerife Island (Canary Islands, Spain). The diverse geographical locations of the sampled beaches across Tenerife broadly represented the archipelago's coastal areas, and enabled a comprehensive analysis of MP contamination in the area. Table 2 presents the general characteristics of the beaches under study, accompanied by information on their specific uses. This table provides valuable insights into the various activities and purposes associated with each beach, which provides the comprehensive understanding of their individual features and functionalities. The sampling period spanned from May 2022 to December 2022, and covered a significant timeframe for data collection (Fig. 1).

The sampling process was conducted above the high tide beach level to collect sand samples. At each beach, 50 × 50 cm quadrats were carefully selected, ensuring a separation distance of 25 m between each quadrat. The top layer of the sand sample, specifically at a depth of 5 cm, was retrieved for further analyses. To isolate the MPs contained in the sand samples, the collected sand was sieved through a mesh (1-millimetre pore size).

In the laboratory, a meticulous approach was adopted to handle the sieved sand samples. Tweezers were utilised to remove any extraneous materials, such as organic matter, rocks, and other residue types. Additionally, pellets and fragments were separated from the rest of the sample. Pellets, which are small and rounded pieces of plastic initially used to manufacture consumer goods, were identified and distinguished from the irregular and generally flat larger fragments that result from the degradation of plastic objects. Careful sample manipulation allowed the precise identification and separation of both pellets and fragments for the subsequent analysis and characterisation.

Table 2
Characteristics of the sampling sites.

Beach	GPS Position	Characteristic
Playa Grande (PG)	28°09.329′ N 16°26.040′ W	Sandy beach, easy access, small town, not very touristic, WWTP in the vicinity
Puertito Adeje (PA)	28°06.521′ N 16°45.680′ W	Sandy beach in a small cove, low water renewal rate, semi-urban, not touristy, micro-reserve of green turtles, WWTP in the vicinity
Playa Diego Hernandez (DH)	28°05.250′ N 16°44.374′ W	Sandy beach, hidden and difficult to access, not very busy, WWTP in the vicinity
Playa Almaciga (A)	28°06.521′ N 16°45.680′ W	Beach of sand and stones, wild but easily accessible, without services, little visited. WWTP in the vicinity
Playa de Tejita (T)	28°34.564′ N 16°19.067′ W	Sandy beach, easy access, small town, very touristic

2.4. Optimization of the extraction and sample preparation

2.4.1. Optimization of the extraction

The extraction process was as follows: six replicas each containing 10 virgin polypropylene pellets (approximately 4 mm diameter) weighing approximately 300 mg ± 30 mg, were spiked with 5 mL of reference solution to achieve a target concentration of 50 ng/mL per analyte. After spiking, pellets were left for 1–2 h until methanol had evaporated. To ensure the most efficient and reproducible extraction of target compounds, several parameters were optimized.

These included the choice of solvent, extraction time, and temperature. The optimization process was conducted using a factorial experimental design using the Minitab® software. The factorial design was conducted in two different stages which allowed for achieving the most suitable combination of the tested values for the different variables that affect the extraction procedure. Following extraction, 1 ml of the extractant containing analytes was transferred to a chromatographic vial for the analysis using the UHPLC-MS/MS system. In those cases, in which suspended solids were observed in extracts, the extractant was transferred to a glass test tube and centrifuged at 3,000 rpm for 10 min before the chromatographic analysis. All analyses were done in triplicate (n = 3). The response peak areas of the individual substances were then calculated.

This mass was also employed for analysing the real samples. Determining sample weight implied considering the variability in MPs distribution because their quantity can significantly vary.

2.4.2. Sample preparation

300 mg ± 30 mg of collected and sieved MP sample were placed inside 10 mL glass vials, and the optimum extraction conditions were applied (5 mL of methanol and a UAE time of 30 min). In most cases, suspended solids were observed in extracts, thus the full volume of methanol containing extracted analytes was transferred to a glass test tube and centrifuged at 3,000 rpm for 10 min before the chromatographic analysis. No filtering or other steps of the centrifuged sample is required. Following extraction, 1 ml of extracted sample was transferred to a chromatographic vial for the analysis using the UHPLC/MS/MS system. All analyses were done in triplicate (n = 3). The response areas of the individual substances were then calculated.

2.5. Chromatographic conditions

Chromatographic separation and analysis were performed in a Phenomenex Kinetex PS C18 analytical column (100 mm × 2.1 mm, 2.6 μm) from Phenomenex (California, USA). Chromatographic separation was carried out in the gradient mode using a mobile phase consisting of water with 5 mM ammonium formate (pH adjusted to 3.2 with formic acid) (A) and methanol with 0.05 % formic acid (v/v) (B). The gradient started with 95 % A and 5 % B maintaining this proportion for 1.0. Then, the composition was gradually changed to 100 % B over the next 6 min. After a 4-minute cleaning step, with 100 % of B, the gradient returned to the initial conditions 95 % A and 5 % B at 12 min, followed by an

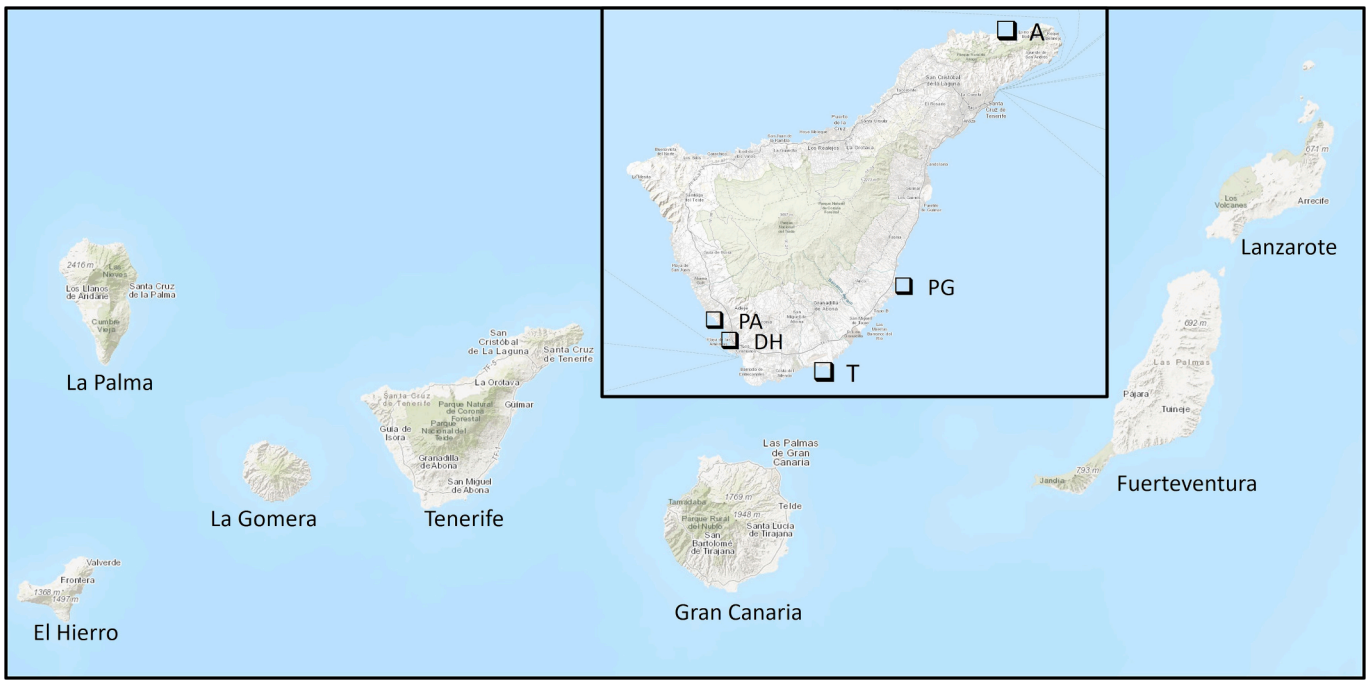

Fig. 1. Location of the beaches studied (Tenerife, Canary Islands, Spain) (Figure taken from google maps).

equilibration step until 15.0 min, and the injected extract volume was 10 μL.

For mass spectrometry detection purposes, the following ESI parameters were employed: a capillary voltage of 3 kV, a radio frequency lens voltage of 2.5 V, an extractor voltage of 3 V, and source and desolvation temperatures set at 150 °C and 500 °C, respectively. The cone gas flow was maintained at 50 L/h, while the desolvation gas flow was set at 600 L/h. Nitrogen served as the desolvation gas and argon was utilised as the collision gas.

The response areas of the individual substances were then calculated. More detailed MS/MS settings for all the analytes, including collision energies, fragmentor voltages, and precursor and product ion transitions, are provided in comprehensive Table 1. These MS/MS settings were optimised for each specific analyte to ensure the optimal fragmentation and detection of the target compounds during the analysis. The precursor and fragment ions were carefully selected to maximise the sensitivity and selectivity for each analyte of interest.

2.6. Analytical parameters

Analytical parameters were calculated for the developed method. The linearity ranges, regression equations and coefficients were determined using least-squares regression analysis, where the peak area response were plotted against the concentration values across the calibration range. To build the calibration curves, five concentration level ranging from 17 to 3,333 ng/g (1–200 ng/mL) were used for most analytes, except sulfmethoxazole, fluconazole and ofloxacin, whose linearity range varied from 84 to 3,333 ng/g (5–200 ng/mL). The signal ratio was plotted against the concentration ratio across the calibration range.

Detection and quantification limits of the whole extraction method (LOD and LOQ, respectively) were evaluated as the concentration that produced signal-to-noise ratios of 3 and 10 respectively, in the quantification ion transition of each compound.

To assess precision, statistical analyses were conducted using six pellet samples weighing approximately 300 mg ± 30 mg, spiked with the target compounds at three concentration levels (25, 50, 100 ng/mL). Precision was quantified as the normalized RSDs for both intraday and interday variations.

3. Results and discussion

3.1. Optimisation of extraction

UAE needs the optimisation of key variables, including extraction time, extractant volume and solvent type. It is crucial to investigate not only the isolated effects of the factors that influence the UAE process, but also the potential interaction effects among these key factors. By examining the interplay among the main factors, a deeper understanding can be gained of how they collectively impact the efficiency and outcomes of the UAE process.

The optimisation process was conducted using a factorial experimental design. The initial experimental design with two-level factorial (3 variables at 2 levels; 2^3) was performed. The variables were as follows: type of solvent (methanol, acetonitrile), extraction times (10 and 30 min) and extractant volumes (5 and 10 mL).

According to the results, the solvent volume was the least influential variable in the extraction, so it was fixed at 5 ml, while other two variables (time and solvent type) are indicating the most significant combination of variables that had the greatest influence during the extraction process.

Next the optimisation of the extraction procedure was performed. A three-level factorial design for two parameters (3^2) was developed for the variables that most affected the process: extraction time and solvent type. During the optimisation process, the extraction times varied at 10, 20 and 30 min. The extractant solvent types were methanol, acetonitrile and ethanol: acetonitrile mixture (50:50, v/v). To minimise carryover effects, runs were randomised to ensure unbiased results. This analysis aimed to determine the optimal combination of these two variables by facilitating the identification of the most effective conditions for the UAE process.

After these two experimental designs, the contour plots of the selected compounds (diflufenican, dimoxystrobin, penconazole; Fig. 2) showed that the shortest extraction time (10 min) yielded lower extraction efficiencies compared to longer durations. A 30-minute extraction time resulted in the highest tested relative recoveries.

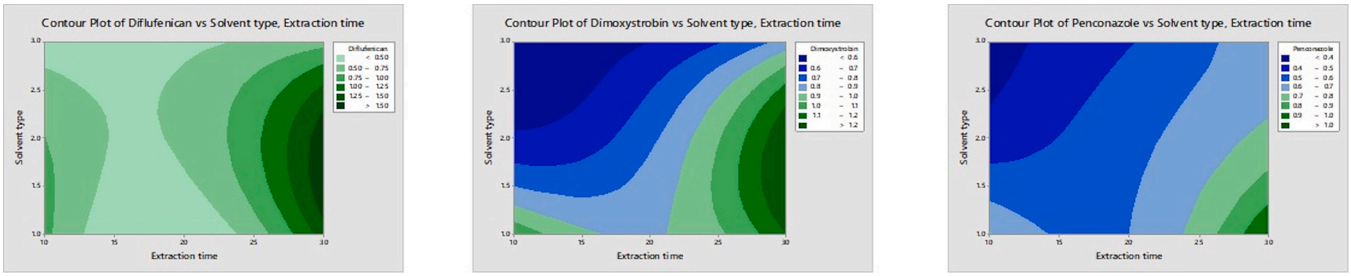

Fig. 2. Contour plot of the selected compounds diflufenican (a), dimoxystrobin (b) and penconazole (c) using MeOH as extractant.

Longer times were not tested to avoid making the extraction time too long. Despite obtaining satisfactory results for all the analytes with the three solvents as extractants, MeOH exhibited the most optimal signal in the detection system. The other compounds exhibited similar behaviour.

Considering these findings, we identified the following conditions as optimal for achieving the highest extraction of the target analytes from the MP samples: methanol (MeOH) was chosen as the extractant, with a solvent volume of 5 mL and an extraction time of 30 min.

Under these optimal conditions, the relative extraction recoveries were calculated. Three hundred milligrams (±30 mg) of virgin polypropylene pellets (10 pellets) were spiked with the target compounds in methanol at three concentration levels: 25, 50, and 100 ng·mL^{-1}. The relative extraction recoveries were calculated for each set of samples, comparing the peak areas of the extracts from spiked pellets with the corresponding "non-adsorbed" concentration of analytes. This can be explained as relative extraction recoveries, because the number of analytes that remained free in the solution or adsorbed on the surface of the laboratory glass was also measured, and this value was subtracted before the evaluation of the extraction efficiency.

As shown in Fig. 3, excellent recoveries were obtained for most compounds, and ranged from 71 % to 106 % for six replicates at all the tested concentrations.

3.2. Analytical parameters and method validation

Following the optimisation of the extraction conditions, the analytical parameters of the UAE-UHPLC-MS/MS method were assessed. The different validation parameters are summarised in Table 3. Under the optimal conditions, the calibration curve showed coefficients of determination (r ^{2}) above 0.99, LODs ranging from 0.03 to 8.55 ng/g and LOQs ranging from 0.07 to 28.50 ng/g. Fig. 4 shows a chromatogram of the separation and identification of the target compounds in the MPs samples at a concentration of 50 ng/mL.

To assess precision, statistical analyses were conducted using six pellet samples spiked with the target compounds at three concentration levels (25, 50, 100 ng/mL). Precision was quantified as the RSDs for both intraday and interday variations. Intraday and interday precisions below 25 % were achieved for every target compound at all the tested levels. Relatively higher RSDs could be explained with the variations within sample weighting. After the normalisation of the concentration and recalculation for analyte per amount of plastic sample, precision significantly improved with RSDs below 15 % for all the studied compounds.

As described in the extraction optimisation section, the normalised relative extraction recoveries varied from 73-106 % (Table 3). More detailed extraction recoveries are shown in Fig. 3 in the form of plot boxes. All six repetitions at the three different concentration levels are included in plots, along with the mean, median, minimum and maximum, and the first and third quartiles.

In the next step, the specificity or influence of the plastic matrix on the measured response of analytes was investigated at three concentration levels: 25, 50, and 100 ng/mL. Blank samples, a pure standard solution containing the analytes, and a model plastic sample, to which the corresponding number of analytes as contained in the standard solution sample was added, were compared. Differences in peak areas were less than 5 % for most analytes, suggesting that the plastic pellets don't exhibit any significant matrix effect. Only famoxadone, avobenzone, octocrylene and ofloxacin showed variations between 11 % and 17 %, indicating a decrease in signal, thus suppression (negative) effect of plastic matrix for these analytes occurred. Hence, the matrix effect was not considered significant.

3.3. Analysis of real samples

The MP samples collected from the five beaches located on the Tenerife Island (Fig. 1) between May and December 2022 were subjected to determine the concentration of the 25 Watch List compounds and to validate the effectiveness of the developed method. Sixty samples were analysed. Samples were divided into fragments and pellets, and three replicates were performed from each sample whenever possible. The compounds detected for all the analysed MP samples are shown in Table 1S. Sixteen of the 25 investigated compounds were detected with varying frequencies on the different sampled beaches. Fig. 5 shows the detection frequencies for the 25 compounds on the Watch List. Detection

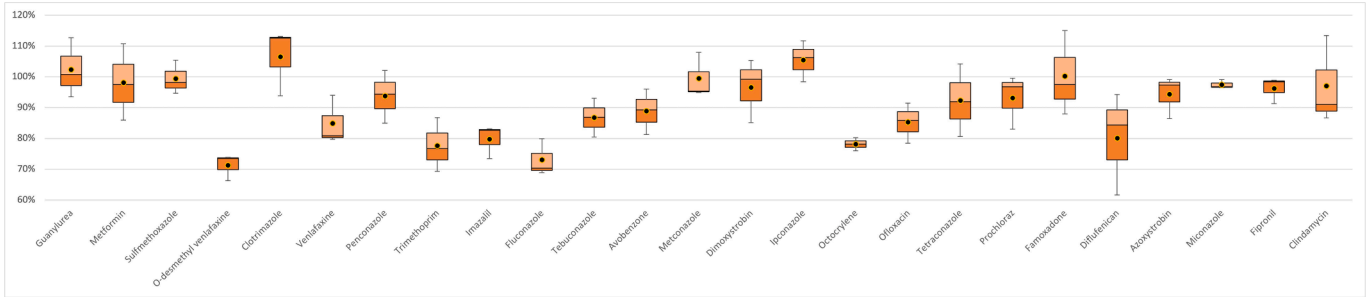

Fig. 3. Relative extraction recoveries of the compounds at three different concentrations (25, 50, 100 ng·ml^{-1}) Plot for each compound contains: the mean (black dot), median, minimum and maximum values and the first quartile (dark orange) and third quartiles (light orange) of recovery values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Analytical parameters: recoveries, intra, inter-day at three levels of concentration.

	Watchlist compounds	LOD/LOQ (ng/g)		Relative Recoveries (%)	Intra-day Precision (norm. %RSD)	Inter-day Precision (norm. %RSD)
1	Guanylurea	0,14	0,48	102 %	6 %	8 %
2	Metformin	0,19	0,62	98 %	11 %	11 %
3	Sulfamethoxazole	8,55	28,50	99 %	9 %	11 %
4	O-desmethyl venlafaxine	0,16	0,53	71 %	8 %	9 %
5	Clotrimazole	0,03	0,09	106 %	6 %	5 %
6	Venlafaxine	0,09	0,31	85 %	12 %	13 %
7	Penconazole	0,06	0,20	94 %	8 %	8 %
8	Trimethoprim	0,45	1,51	78 %	6 %	8 %
9	Imazalil	0,21	0,71	80 %	11 %	13 %
10	Fluconazole	1,10	3,65	73 %	13 %	14 %
11	Tebuconazole	0,07	0,22	87 %	3 %	5 %
12	Avobenzone	1,24	4,12	89 %	13 %	14 %
13	Metconazole	0,10	0,32	99 %	5 %	6 %
14	Dimoxystrobin	0,06	0,19	97 %	9 %	9 %
15	Ipconazole	0,08	0,27	105 %	6 %	7 %
16	Octocrylene	0,52	1,72	78 %	13 %	15 %
17	Ofloxacin	4,28	14,27	85 %	8 %	10 %
18	Tetraconazole	0,15	0,51	92 %	9 %	10 %
19	Prochloraz	0,05	0,17	93 %	8 %	9 %
20	Famoxadone	0,26	0,88	100 %	6 %	8 %
21	Diflufenican	0,75	2,49	80 %	10 %	13 %
22	Azoxystrobin	0,07	0,24	94 %	5 %	7 %
23	Miconazole	0,09	0,31	97 %	7 %	7 %
24	Fipronil	0,35	1,16	96 %	9 %	11 %
25	Clindamycin	0,03	0,07	97 %	8 %	10 %

Note: Relative extraction recoveries and Intra-day and Inter-day precisions calculated from six replicates at three different concentration levels (25, 50, 100 ng/mL).

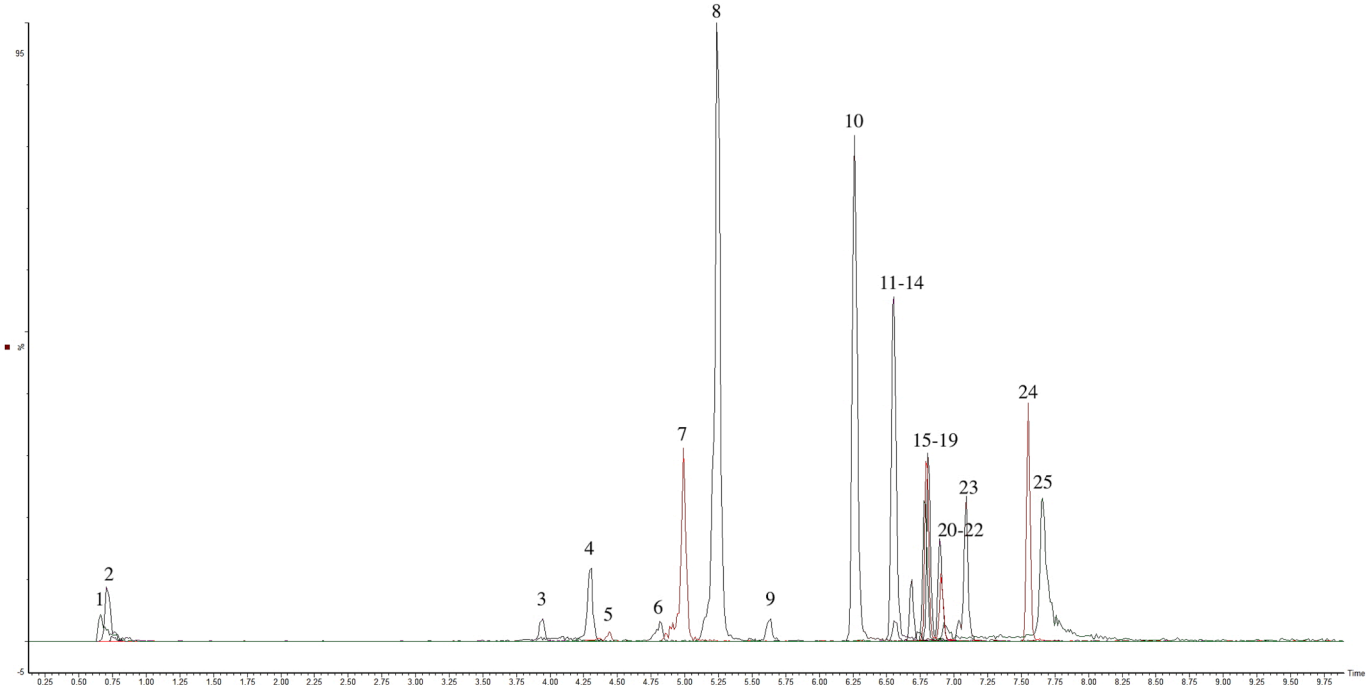

Fig. 4. Chromatogram of target compounds obtained using UAE-UHPLC-MS/MS method The numbered peaks correspond to the identified compounds: 1. Guanylurea, 2. Metformin, 3. Trimethoprim, 4. Sulfmethoxazole, 5. O-desmethyl venlafaxine, 6. Ofloxacin, 7. Fluconazole, 8. Venlafaxine, 9. Clindamycin, 10. Imazalil, 11. Azoxystrobin, 12. Tetraconazole, 13. Clotrimazole, 14. Fipronil, 15. Dimoxystrobin, 16. Tebuconazole, 17. Penconazole, 18. Famoxadone, 19. Metconazole, 20. Miconazole, 21. Prochloraz, 22. Diflufenican, 23. Ipconazole, 24. Octocrylene, 25. Avobenzone.

frequencies ranged from 1.7 % for clotrimazole to 83.3 % for octocrylene. However, only five compounds were quantified because the other detected compounds were below their LOQs.

Octocrylene was the most commonly detected compound at the several sampled locations. Its concentration ranged from 22 to 824 ng/g. Abnormally high results were found in the samples from the La Tejita Beach in July (4,357 ng/g), and from Puertito de Adeje in May (4,635 ng/g). Taking into account that octocrylene is a compound that is commonly used in PCPs formulations and Tejita is a well-known tourist beach, the higher measured concentration in July is not very surprising and may be related to a large number of swimmers. However, as Puertito Adeje is no such tourist place, its higher octocrylene concentration may be due to the presence of a nearby wastewater treatment plant. Occurrence and the concentration range of Octocrylene correlate with the

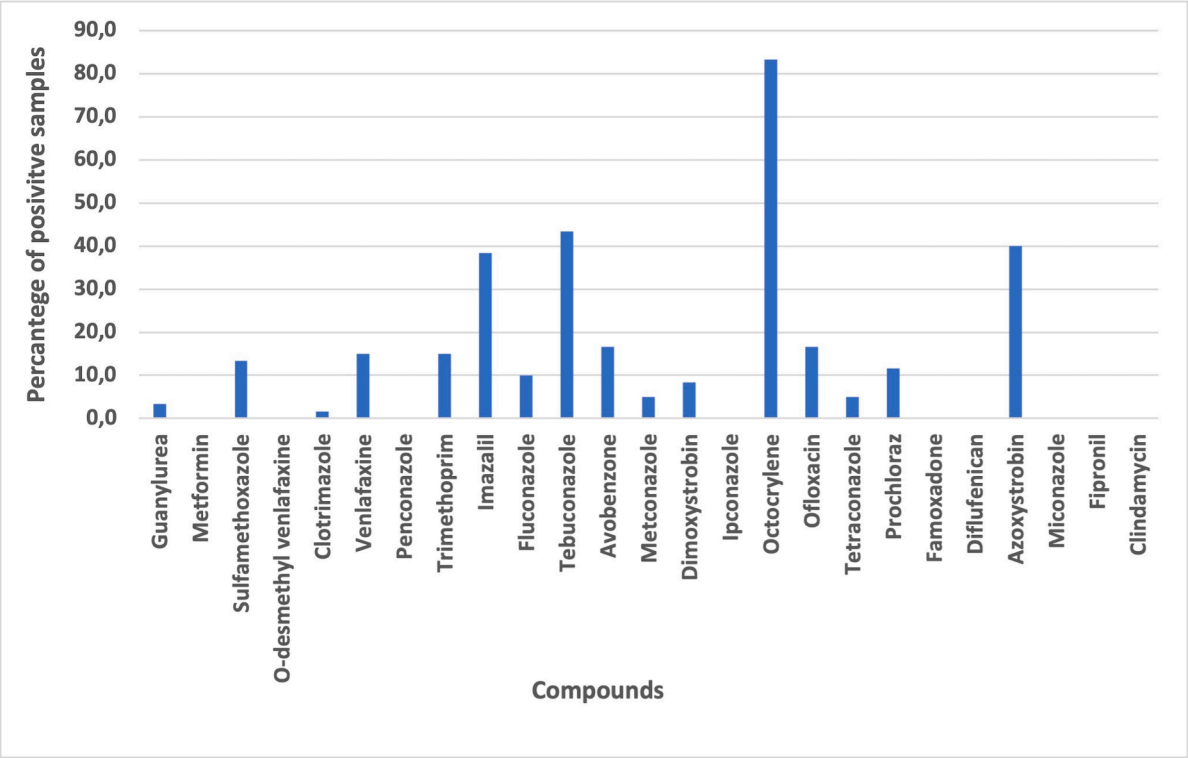

Fig. 5. Detection frequencies of the compounds studied.

previous findings in the work of Santana-Viera et al. [27] in microplastic debris from the Canary Islands.

In addition to octocrylene, another UV filter (avobenzone) was detected in 16.7 % of the samples, and was quantified in two: in the fragment samples from Playa Grande (May 2022, 112 ng/g) and in the pellet samples from Puertito de Adeje (May 2022, 105 ng/g). Both samples had avobenzone concentrations over the LOQ of the analytical method. However, its concentration and abundance in samples were considerably lower than for octocrylene.

Outside this group of substances, some samples (38.3 %) contained imazalil, a fungicide used in citrus cultivation. It was quantified in only one fragment sample taken in May from Puertito Adeje (34 ng/g). Another compound quantified in only one sample (1.7 %) was clotrimazole, which is an antifungal compound used for fungal infections. It was determined in the fragment samples from Playa Tejita (15 ng/g). Ofloxacin is a broad-spectrum antibiotic. It was detected in 16.7 % of the samples and quantified in only one sample of the fragment samples from Puertito Adeje (84 ng/g). According to the low frequency of detection of these last two compounds (1.7 % and 16.7 %, respectively), it was not easy to certainly demonstrate their recurrence in the monitored samples.

Other compounds, such as tebuconazole and azoxystrobin (fungicides used in agricultural or gardening), respectively had a detection frequency of 43.3 % and 40 %. Nevertheless, they were not quantified because their concentrations were lower than the LOQs.

Regarding beaches, Almáciga was where the most compounds were detected and where some positive results were obtained for 91 % of the samples. However, only octocrylene was quantified. This is not considered a very tourist place, it is located to the north of Tenerife and is primarily used for surfing. It is close to agricultural areas and a wastewater treatment plant. The presence of more compounds may require special attention being paid in environmental monitoring and management terms to ensure the quality and safety of this beach and its surroundings.

Table 4 shows the total number of compounds detected on each beach and every kind of MP sample. More compounds were detected in the plastic fragment samples than pellets, in all the beach samples and throughout all the months. This can be attributed to the rougher and, therefore, more accessible surface to adsorb analytes on the sample surface. A similar conclusion has been reached by others works, such as Tourinho et al. [9] and Xiao Lin et al. [24].

Unfortunately, as we did not obtain enough samples from each beach during the complete monitoring period, it was not possible to estimate the overall effect of the tourist season on the concentration of the analytes in samples.

It is important to recognize that certain contaminants, such as UV filters, plasticizers or flame retardants could originate from microplastics themselves, as they are often added as additives during the production of plastic products. However, other contaminants, not originally part of the microplastic composition, may be adsorbed from the surrounding environment, further complicating the determination of

Table 4
Total number of compounds detected at each beach and in each sampling.

	May-2022		Jul-2022		Sep-2022		Dec-2022	
	Fragments	Pellets	Fragments	Pellets	Fragments	Pellets	Fragments	Pellets
Playa Grande	5	n/d	n/d	n/d	n/d	n/d	n/d	n/d
Tejita	13	12	13	9	n/d	9	n/d	n/d
Puertito Adeje	13	5	n/d	16	12	n/d	n/a	n/a
Almáciga	11	9	13	7	13	n/d	8	n/d
Diego Hernández	n/d	n/d	9	5	14	n/d	n/d	n/d

contamination sources. The combination of these two factors—contaminants being adsorbed from the environment and those originally present in the plastic products—complicates the identification of the primary source.

Based on the occurrence of organic pollutants across various beaches with different geographical locations on the island, as well as the distribution of tourism and other industries, we hypothesize that the primary source of contamination is the pollution of coastal waters, with these substances being subsequently adsorbed onto microplastics. To better understand the dynamics between these two sources, we plan to conduct longer-term studies, including analyses of wastewater samples, to verify these hypotheses.

4. Conclusions and future trends

Pollutants adsorbed onto MPs are a growing concern. Numerous studies have shown that MPs can adsorb priority pollutants, whose concentrations are sometimes higher than those in the surrounding environment. There are a variety of factors that influence the adsorption process. This process depends on the type and composition of the MPs, as well as the particle size, shape, and aging state of the materials. Additionally, the physicochemical properties of organic pollutants, such as polarity and ionic characteristics, are critical factors in the adsorption process. Environmental factors, including pH, temperature, and UV radiation, also play an important role in the adsorption capacity of MPs. However, the extent of the emerging pollutants issue, specifically emerging organic compounds, is still uncertain. Limited research has focused on developing techniques to extract these pollutant types from MPs despite many scientific articles having focused on an interaction mechanism between these compounds and MPs materials.

In this study, we optimised a UAE-UHPLC-MS/MS method that utilises ultrasound energy to extract 25 compounds from the latest EU Watch List from MPs belonging to different groups before their determination by UHPLC-MS/MS. We also tested the proposed methodology to meet validation criteria. Under optimal conditions, we achieved normalised relative standard deviations below 15 % for most compounds, with LODs ranging from 0.03 ng/g to 8.55 ng/g.

The developed methodology was applied to analyse the MP samples collected from five Tenerife beaches. Several emerging organic compounds on the EU Watch List were detected to be adsorbed on MPs. Detection frequencies ranged from 1.7 % for clotrimazole to 83.3 % for octocrylene. Their concentrations ranged from 15 to 824 ng/g. The obtained results revealed that MPs have a high adsorption capacity of different groups of compounds, such as fungicides, pharmaceuticals or personal care products.

This study represents a significant advance in knowledge about the distribution of the adsorption of emerging organic pollutants on MPs, which can contribute to a better environmental risk assessment associated with these materials. However, as the study was carried out on a limited number of samples, more extensive studies are required to include more samples and environmental conditions.

CRediT authorship contribution statement

Ludovit Schreiber: Writing – original draft, Methodology, Investigation. **Nicolas Milan Michalides:** Methodology, Investigation. **Zoraida Sosa-Ferrera:** Writing – review & editing, Writing – original draft, Conceptualization. **José Juan Santana-Rodríguez:** .

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ludovit Schreiber reports was provided by European Union Grant Agreement No. 101090291. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Ludovit Schreiber would like to thank Grant Agreement No. 101090291 funded by the European Union. The authors thanks the ACHEM - Applied Analytical Chemistry Group from the University of La Laguna for supplying the MPs samples obtained on Tenerife beaches (Project MAC 2/1.1[a]/265 (IMPLAMAC)).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2024.111987.

Data availability

Data will be made available on request.

References

[1] R. Geyer, J.R., Jambeck, K.L., Law, 2017. Production, use, and fate of all plastics ever made. Sci. Adv. 3, e1700782 https://doi.org/10.1126/sciadv.1700782.
[2] Y. Picó, D. Barceló, Analysis and Prevention of Microplastics Pollution in Water: Current Perspectives and Future ACS, Omega 4 (4) (2019) 6709–6719, https://doi.org/10.1021/acsomega.9b00222.
[3] F. Wang, C.S. Wong, D. Chen, X. Lu, F. Wang, E.Y. Zeng, Interaction of toxic chemicals with microplastics: a critical review, Water Res. 139 (2018) 208e219, https://doi.org/10.1016/j.watres.2018.04.003.
[4] G. Erni-Cassola, V. Zadjelovic, M.I. Gibson, J.A. Christie-Oleza, Distribution of plastic polymer types in the marine environment; A meta-analysis, J. Hazard. Mater. 369 (2019) 691–698, https://doi.org/10.1016/j.jhazmat.2019.02.067.
[5] A.L. Andrady, The plastic in microplastics: a review, Mar. Pollut. Bull. 119 (2017) 12–22, https://doi.org/10.1016/J.MARPOLBUL.2017.01.082.
[6] R. Guedes-Alonso, S. Montesdeoca-Esponda, J. Pacheco-Juárez, Z. Sosa-Ferrera, J. J., Santana-Rodríguez, 2020. A survey of the presence of pharmaceutical residues in wastewaters. Evaluation of their removal using conventional and natural treatment procedures. Molecules 25, 1639. https://doi.org/10.3390/molecules25071639.
[7] P.G Ryan, C.J, Moore, J.A., van Franeker, C.L, Moloney, 2009. Monitoring the abundance of plastic debris in the marine environment. Philos. Trans. R. Soc. B Biol. Sci. 364, 1999e2012. https://doi.org/10.1098/rstb.2008.0207.
[8] D. Eerkes-Medrano, R.C. Thompson, D.C. Aldridge, Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs, Water Res. 75 (2015) 63–82, https://doi.org/10.1016/J.WATRES.2015.02.012.
[9] P.S. Tourinho, V. Ko9cí, S. Loureiro, C.A.M. van Gestel, 2019. Partitioning of chemical contaminants to microplastics: sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation, Environ. Pollut. 252, 1246–1256, doi:https://doi.org/10.1016/j. envpol.2019.06.030.
[10] F. Yu, C. Yang, Z. Zhu, X. Bai, J. Ma, Adsorption behavior of organic pollutants and metals on micro/nanoplastics in the aquatic environment, Sci. Total Environ. 694 (2019) 133643, https://doi.org/10.1016/j. scitotenv.2019.133643.
[11] Q. Chen, J. Reisser, S. Cunsolo, C. Kwadijk, M. Kotterman, M. Proietti, B. Slat, F. F. Ferrari, A. Schwarz, A. Levivier, D. Yin, H. Hollert, A.A. Koelmans, Pollutants in plastics within the North Pacific Subtropical gyre, Environ. Sci. Technol. 52 (2) (2018) 446–456, https://doi.org/10.1021/acs.est.7b04682.
[12] H. Hirai, H. Takada, Y. Ogata, R. Yamashita, K. Mizukawa, M. Saha, C. Kwan, C. Moore, H. Gray, D. Laursen, E.R. Zettler, J.W. Farrington, C.M. Reddy, E. E. Peacock, M.W. Ward, Organic micropollutants in marine plastics debris from the open ocean and remote and urban beaches, Mar. Pollut. Bull. 62 (2011) 1683–1692, https://doi.org/10.1016/j.marpolbul.2011.06.004.
[13] I. Bashir, F.A. Lone, R.A. Bhat, S.A. Mir, Z.A. Dar, Concerns and threats of contamination on aquatic ecosystems, in: Bioremediation and Biotechnology: Sustainable Approaches to Pollution Degradation, Springer International Publishing, 2020, pp. 1–26, https://doi.org/10.1007/978-3-030-35691-0_1.
[14] Directives Directive 2013/39/EU of The European Parliament and of The Council amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.
[15] Commission Implementing Decision (EU) 2015/495 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.
[16] Commission Implementing Decision (EU) 2022/1307 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.
[17] G. Cortes, N. Cuenca, & P.Rodriguez, (n.d.). Factsheets of the substances for the 4 th Watch List under the Water Framework Directive Annex II. https://doi.org/10.2760/71717.

[18] A. Grobin, R. Roškar, J. Trontelj, Multi-parameter risk assessment of forty-one selected substances with endocrine disruptive properties in surface waters worldwide, Chemosphere 287 (2) (2022) 132195, https://doi.org/10.1016/j.chemosphere.2021.132195.
[19] L. Fu, J. Li, G. Wang, Y. Luan, W. Dai, Adsorption behaviour of organic pollutants on microplastics, Ecotoxicol. Environ. Saf. 217 (2021) 112207, https://doi.org/10.1016/j.ecoenv.2021.112207.
[20] X. Song, W. Zhuang, H. Cui, M. Liu, T. Gao, A. Li, Z. Gao, Interactions of microplastics with organic, inorganic and bio-pollutants and the ecotoxicological effects on terrestrial and aquatic organisms, Science of The Total Environment, Volume 838, Part 2, ISSN 156068 (2022) 0048–9697, https://doi.org/10.1016/j.scitotenv.2022.156068.
[21] J. Li, K. Zhang, H. Zhang, Adsorption of antibiotics on microplastics, Environmental Pollution, Volume 237, ISSN 460–467 (2018) 0269–7491, https://doi.org/10.1016/j.envpol.2018.02.050.
[22] Y. Leng, W. Wang, H. Cai, F. Chang, W. Xiong, J. Wang, Sorption kinetics, isotherms and molecular dynamics simulation of 17β-estradiol onto microplastics, Science of The Total Environment, Volume 858, Part 3, ISSN 159803 (2023) 0048–9697, https://doi.org/10.1016/j.scitotenv.2022.159803.
[23] G.A. Elizalde-Velázquez, L.M. Gómez-Oliván, S. García-Medina, M. Hernández-Díaz, H. Islas-Flores, M. Galar-Martínez, A.L. García-Medina, J. J. Chanona-Pérez, J.D. Hernández-Varela, 2022. Polystyrene microplastics mitigate the embryotoxic damage of metformin and guanylurea in Danio rerio, Science of The Total Environment, Volume 852, 158503, ISSN 0048-9697, ttps://doi.org/10.1016/j.scitotenv.2022.158503.
[24] X. Liu, D.D. Zhou, M. Chen, Y.W. Cao, L.Y. Zhuang, Z.H. Lu, Z.H. Yang, Adsorption behaviour of azole fungicides on polystyrene and polyethylene microplastics, Chemosphere 308 (2) (2022) 136280, https://doi.org/10.1016/j.chemosphere.2022.136280.
[25] S. Santana-Viera, S. Montesdeoca-Esponda, M.E. Torres-Padrón, Z. Sosa-Ferrera, J. J. Santana-Rodríguez, An assessment of the concentration of pharmaceuticals adsorbed on microplastics, Chemosphere 266 (2021) 129007, https://doi.org/10.1016/j.chemosphere.2020.129007.
[26] S.H. Hong, W.J. Shim, L. Hong, Methods of analysing chemicals associated with microplastics: a review, Anal. Methods. (2017), https://doi.org/10.1039/c6ay02971j.
[27] 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.
[28] R. Guedes-Alonso, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Analysis of microplastics-sorbed endocrine-disrupting compounds in pellets and microplastic fragments from beaches, Microchem. J. 171 (2021) 106834, https://doi.org/10.1016/j.microc.2021.106834.
[29] J. Li, K. Zhang, H. Zhang, Adsorption of antibiotics on microplastics, Environ. Pollut. 237 (2018) 460–467.
[30] M. Llorca, M. Farré, H.K. Karapanagioti, D. Barceló, Levels and fate of perfluoroalkyl substances in beached plastic pellets and sediments collected from Greece, Mar. Pollut. Bull. 87 (1–2) (2014) 286–291, https://doi.org/10.1016/j.marpolbul.2014.07.036.
[31] B. Albero, C. Sánchez-Brunete, A.I. García-Valcárcel, R.A. Pérez, J.L. Tadeo, Ultrasound-assisted extraction of emerging contaminants from environmental samples, TrAC Trends Anal. Chem. 71 (2015) 110–118, https://doi.org/10.1016/j.trac.2015.03.015.