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Fate and distribution of benzotriazole UV filters and stabilizers in environmental compartments from Gran Canaria Island (Spain): A comparison study

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ABSTRACT

Tourism is an economic sector of great importance worldwide. In coastal areas, this activity is associated with the use of personal care products, such as ultraviolet (UV) filters and stabilizers. Therefore, assessing their presence and the exposure of living organisms to the impact of this kind of pollutant in such areas could be especially important. The Canary Islands (Spain) are considered an outermost region, and their main economic activity is based on tourism, both national and international. Thus, this area could be remarkably vulnerable to this kind of pollution, and its characterization could be useful to infer conclusions for other similar regions.With this aim, the occurrence of organic UV filters and stabilizers in different environmental matrices in Gran Canaria Island is presented in this work. Six benzotriazole compounds, UV-P, UV-326, UV-327, UV-328, UV-329 and UV-360, were found in wastewater, seawater, sludge, sediment, seaweed and fish samples. The numerous studies devoted to establishing the distribution of these target compounds in many different matrices on a touristic and particularly overcrowded island such as Gran Canaria can be used to understand the pollution situation in similar locations. The works in which determination procedures using different extraction techniques were optimized and validated for the analysis of liquid and solid samples are summarized. They are critically discussed regarding their characteristics and analytical parameters.This research is of interest to environmental managers specializing in the conservation of coastal areas where tourism is an important industry since the active components of UV filters and stabilizers can bioaccumulate and biomagnify in the trophic chain.

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1. Introduction

Coastal and maritime tourism is an important sector and has been identified as an emerging area by the Blue Growth strategy of the European Union (EU). Furthermore, the EU considers the optimization of the use of oceans and seas a priority to guarantee the development and sustainable growth of coastal regions and, therefore, allow Europe to be maintained and consolidated as the main tourist destination in the world (Tovar-Sánchez et al., 2019).

Within the EU, the Canary Islands are considered an outermost region, with the main economic activity being tourism, both national and international. Visitors arrive throughout the year looking for sun and rest at beaches and pools. According to the Canary Institute of Statistics, the archipelago, formed by 8 islands, received 15,112,288 tourists in 2019, of which 4,267,384 correspond to Gran Canaria Island (ISTAC, 2019). The location of the archipelago and the studied island in Europe is shown in Fig. 1. The use of personal care products (PCPs) associated with sun protection in coastal tourism activities (sunbathing at the beach, water sports and activities, etc.) has increased exponentially. Hence, the impact of these kinds of pollutants on the coast could be especially important.

The pollution of aquatic ecosystems, especially oceans and seas, is an issue of growing concern for scientists as well as for populations. However, attention is generally focused on the damage that garbage, such as plastics and microplastics, causes in organisms. Nevertheless, flora and fauna are also affected by the micropollutants that are present in the water. Different chemical compounds can reach marine ecosystems, mainly through the effluents of wastewater treatment plants (WWTPs) (Pesqueira et al., 2020). PCPs are an interesting group due to the huge variety of products and their wide daily use (Wang et al., 2017). Among them, ultraviolet (UV) filters and stabilizers are added to sunscreens to protect the skin against UV light, as well as their use in hair dyes, creams and a variety of cosmetics (Apel et al., 2018a). Therefore, they can enter the marine ecosystem not only through the effluents of WWTPs but also directly by means of bathers on beaches or by discharges from swimming pools (Teo et al., 2015). Moreover, some of these compounds are employed in plastics, such as food packaging materials, to avoid sunlight degradation (Hu et al., 2019). This means that microplastic fragments could also be a source of pollution. Thus,

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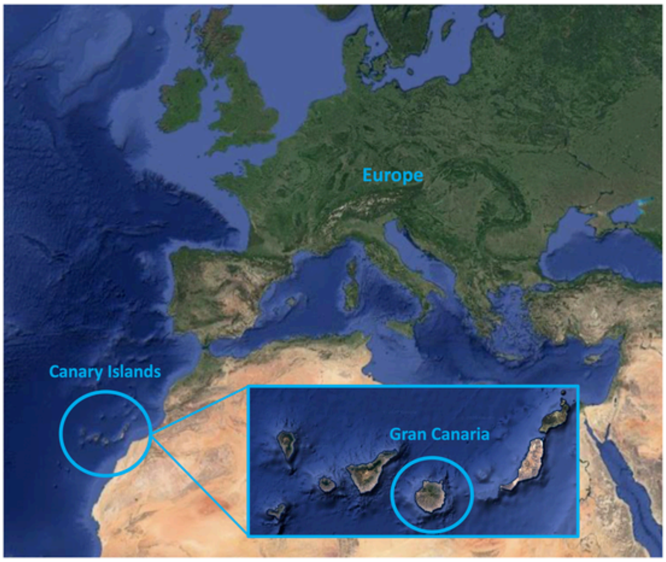

Fig. 1. Location of Gran Canaria island (developed from Google Maps).

very touristic coastal areas can become very vulnerable to this kind of pollution (Tovar-Sánchez et al., 2019).

UV filters and stabilizers have been detected in different marine compartments worldwide, such as waters and marine sediments (Cadena-Aizaga et al., 2020; Montesdeoca-Esponda et al., 2013c). However, the greatest concern is that they have also been found in different levels of the trophic chain (Montesdeoca-Esponda et al., 2018). Although there is not as much literature as for other pollutant compounds, it has been demonstrated that some UV filters and stabilizers are toxic and endocrine-disrupting for different marine organisms (Bilal et al., 2020).

A variety of marine animals, from small crustaceans to large mammals, have accumulated both UV filters (Bachelot et al., 2012; Emnet et al., 2015; Gago-Ferrero et al., 2013; Langford et al., 2015; Picot Groz et al., 2014; Sang and Leung, 2016) and UV stabilizers (Kim et al., 2011a, 2011b; Nakata et al., 2012, 2010, 2009; Peng et al., 2015). Although the concentrations detected are generally low, on the order of magnitude of ng g^{-1}, the presence of these compounds in the trophic chain results in a risk of biomagnification.

Owing to the low concentrations of these compounds in environmental compartments as well as the complexity of samples, selective and sensitive separation and detection techniques, such as liquid chromatography coupled to mass spectrometry, are mandatory in this kind of analysis. Furthermore, previous extraction, clean-up and preconcentration procedures are normally needed.

In this work, a summary of the occurrence of benzotriazole UV filters and stabilizers in Gran Canaria Island (Spain) is provided. Moreover, the variety of analytical methods optimized, validated and applied to determine the target compounds in different types of matrices have been reviewed. Conventional extraction techniques, microextraction approaches, and an automatized procedure have been employed. Such studies encompass different environmental matrices: i) influent and effluent of wastewaters, ii) seawater, iii) sludge, iv) marine sediments, v) seaweed and vi) fish. Additionally, studies in two different aquatic habitats, beaches and marine outfall areas, have been considered. The occurrence of target compounds on Gran Canaria Island is also compared with that found in other locations worldwide.

Six benzotriazole derivatives (Fig. 2) are included in the comparative study. The benzotriazole molecule ($C_6H_5N_3$) has a heterocyclic structure, while its derivatives have an attached phenolic group that absorbs the full UV-A and UV-B spectra. The studied analytes have a wide range of polarities (values of log K_{ow} between 2.998 and 12.46), which, as shown later, could have a great influence on the obtained extraction efficiencies.

To the best of our knowledge, it is not common to have information about the occurrence of a specific group of pollutants in so many different matrices from the same location, in this case a very touristic island. The suitable characterization of benzotriazole compounds in the different environmental compartments of such singular regions could be of interest in the management of coastal areas with tourism as the main activity.

Given the growing concern about the conservation of these marine areas regarding the pollution caused by sunscreens, this work could be used as a valuable tool to determine their fate and distribution in other touristic and overcrowded regions.

2. Analysis procedures

Different approaches have been developed for the determination of target analytes in the study area. All steps of the employed analytical procedures are reviewed below, and the advantages and disadvantages of the different extraction techniques used are critically discussed. The quality control of the developed methods is also reviewed, and the summary of optimized conditions and analytical parameters (extraction efficiencies, precision expressed as relative standard deviation, along with limits of detection and quantification) are shown in Table 1.

2.1. Sampling and conservation

The correct selection of sampling locations as well as appropriate manipulation and conservation of the samples are mandatory to obtain reliable results in the analysis. Discrete or composite samples must be chosen in a way that ensures the representativeness of the sampling. The use of adequate sampling materials according to the matrix and target analytes must also be taken into account. Then, the samples must be kept cold until storage in the laboratory.

Liquid samples (influent and effluent of wastewaters and seawater) were collected in glass amber bottles. In the case of seawater from beaches, the samples were collected at a depth of approximately 1 m. In areas influenced by marine outfalls, seawater was taken from the surface and at a deep level by a professional diver. Then, they were filtered through 0.2 μm filters to eliminate the suspended particles and stored at 4 °C. If the samples were not analysed immediately, they were acidified at pH between 2.5 and 3 to prevent the growth of microorganisms.

Solid samples (sludges from WWTPs and marine sediments) were taken in glass bottles, freeze-dried, sieved to homogenize and stored at −20 °C until analysis. For the sampling of sediments from beaches, low tide was selected, and samples were taken where the waves reached the shore. Sediments near marine outfalls were collected at depths of 15–20 m by a professional diver.

Regarding biota, seaweed samples were collected at low tide and carefully washed with Milli-Q water to remove salt and sand before extraction. Fish samples were collected by a professional underwater fisherman, and the parts of interest, muscle and viscera, were manually separated. Seaweed and fish samples were then freeze-dried, triturated, sieved and stored at 4 °C until analysis.

2.2. Extraction and clean-up

Liquid and solid samples, especially environmental samples, require extraction and clean-up steps to isolate the target analytes and remove interferences. The application of a purification method often also provides a preconcentration of the samples, allowing the low

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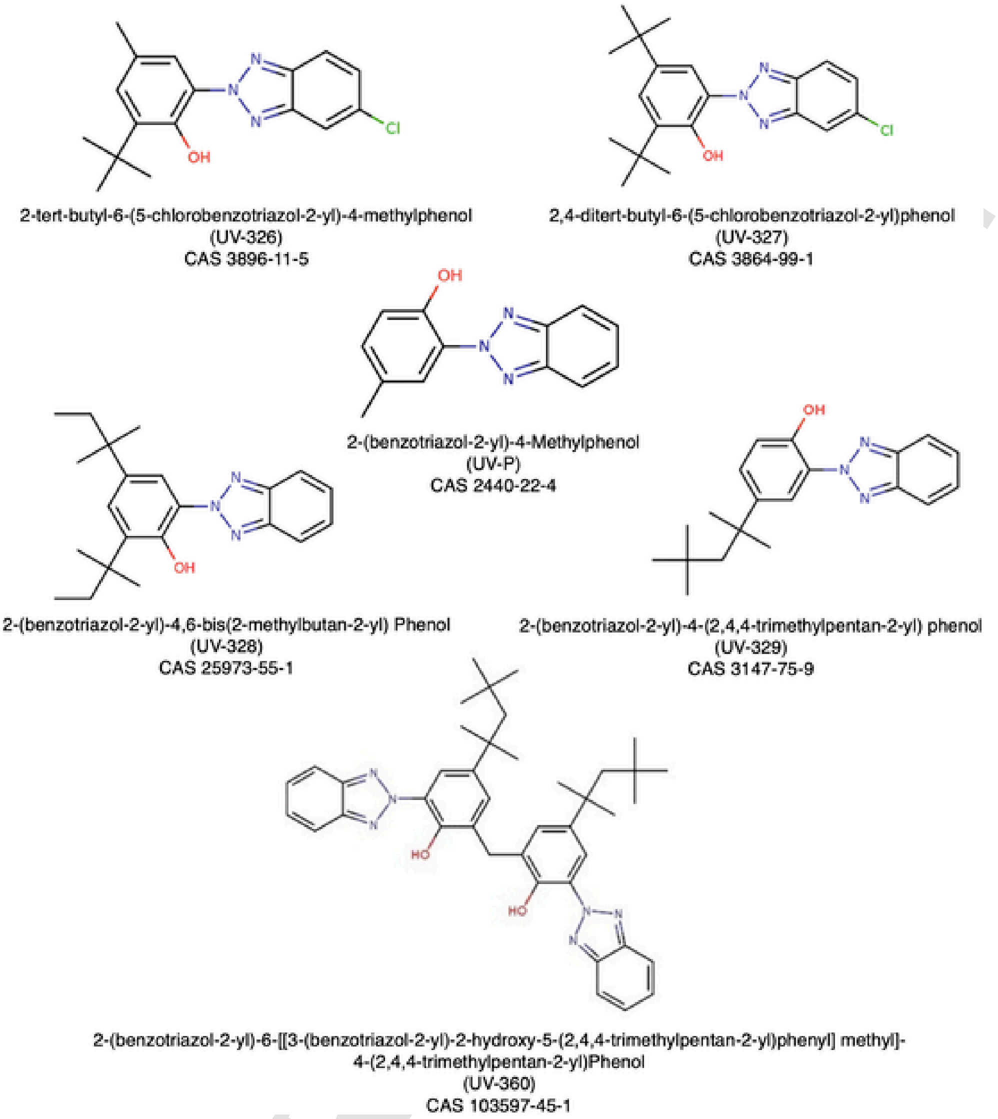

Fig. 2. Analysed benzotriazole derivative compounds in the reviewed papers.

detection limits required for micropollutants to be reached. In all cases, this optimized step was followed by ultra-high-performance liquid chromatography with tandem mass spectrometry detection, as described in detail in the next section.

2.2.1. Off-line solid phase extraction

Conventional solid phase extraction (SPE) is probably the most commonly used technique for the extraction of liquid samples (Buszewski and Szultka, 2012). The availability of many different sorbents makes it a suitable technique for pollutants with very varied characteristics. Moreover, its cost is relatively low, so it is affordable for most laboratories.

An off-line SPE procedure was optimized to analyse benzotriazole derivatives in wastewater and seawater samples (Montesdeoca-Esponda et al., 2012). Different parameters were optimized, starting with the sorbent. Oasis HLB (200 mg) was selected, a hydrophilic lipophilic balance material that allows the extraction of compounds over a wide range of pH values. Then, sample volume, sample pH, washing steps and elution were also studied using an experimental design that allows studying the influence of each variable and the relationship between them. The optimum conditions for each matrix, wastewater and seawater are shown in Table 1.

Although the commercially available devices for this technique allow the simultaneous extraction of up to 20 samples, the handling of such a number of samples is very difficult. The low volume of the cartridge makes it necessary to fill it continuously, and more than 6–8 samples cannot be attended at the same time. Moreover, small differences in the flow rate, which is also set manually, could influence the precision of the method. In this case, the precision ranged between 9 and 13%, which was slightly higher for wastewater than for seawater due to interference.

Satisfactory extraction efficiencies were achieved, higher than 70% for almost all the compounds. Lower recoveries were obtained for the more non-polar compounds, probably due to their strong retention in the sorbent. The achieved preconcentration factor (50) allows adequate LODs for these samples (from 5.4 to 18 ng·L^{-1}) to be achieved.

2.2.2. On-line solid phase extraction

Automatization is an important approach that allows improving the characteristics of extraction techniques. In the case of SPE, the on-line mode coupled with a chromatographic system solves some drawbacks of conventional procedures (Núñez et al., 2012). The most important is related to the minimal handling of the sample,

Table 1
Comparison of the methods used for the determination of benzotriazole derivatives in liquid samples. All the extraction techniques were followed by UHPLC-MS/MS.

Extraction technique	Matrix	Sample volume (mL)	Time (min)	Extractant, volume (mL)	Extraction efficiency (%)	Precision (RSD, %)	LODs ($ng{\cdot}L^{-1}$)	LOQs ($ng{\cdot}L^{-1}$)	Ref.
Off-line SPE	Wastewater	100	30	Methanol, 2	56–82	9.1–13	5.4–18	18–60	Montesdeoca-Esponda et al., 2012
	Seawater				60–89	9.0–12	5.3–17	18–57	
On-line SPE	Wastewater	5	5	Methanol with 0.1% of formic acid at 0.6 mL min^{-1}	58–90	6.2–10	1.1–4.5	3.7–15	
	Seawater				61–94	6.5–9	0.9–4.4	3.0–15	
SBSE	Wastewater	25	140	Acetonitrile, 1.5	18–83	8–13	19–55	63–183	Montesdeoca-Esponda et al., 2013a
	Seawater				18–92	6.5–10	18–51	60–170	
FPSE	Wastewater	10	65	Methanol, 1	35–99	7.7–29	6.6–61	22–203	Montesdeoca-Esponda et al., 2015
	Seawater	25	160		9.3–46	3.9–10	2.7–9.0	9.0–30	García-Guerra et al., 2016

which avoids losses, contamination and reproducibility problems. All the procedures (sample loading, elution and wash) were performed automatically, minimizing the manual errors and improving the precision. Moreover, the analyst employs less time in the manual part of the analysis, an important issue in routine laboratories with a high number of samples. In the on-line method developed for the six target benzotriazole derivatives in wastewater and seawater matrices, the extraction and detection procedures were performed in only 5 min (Montesdeoca-Esponda et al., 2012).

The required volume of sample to obtain an adequate instrumental signal is also lower (in this case, 5 mL) because the elution is carried out with the mobile phase. This means that all the analytes reach the detector, while, in off-line SPE, only some μL volume of the extract is injected into the system. This raises some singularities, for example, that the recoveries must be calculated in terms of mass instead of concentration. As Table 1 shows, the extraction efficiencies obtained in the determination of target benzotriazole derivatives were slightly better in on-line than in off-line SPE. However, the same trend was observed for the most non-polar compound, UV-360 (Log K_{ow} 12.46), for which the recovery was lower, 65%. The factor of preconcentration in on-line SPE is also higher than that achieved in off-line mode (500 vs 50 times), which provides lower LODs, between 0.9 and 4.5 $ng{\cdot}L^{-1}$.

Despite the multiple advantages of on-line procedures, some drawbacks must also be taken into account. The first is the cost of the installation. Several modifications are needed in the chromatographic system and software to carry out the on-line approach. Another disadvantage is the poor availability of different sorbents in comparison with the off-line mode. They are packaged in direct connect columns, and the most commonly used is Oasis HLB due to its wide applicability to different compounds. Hence, it was selected for the extraction of benzotriazole derivatives. On the other hand, although the procedure per sample is faster, it is not possible to extract more than one sample at the same time. In the procedure developed for the benzotriazole derivatives, the equipment possesses two extraction columns in which a sample is charged while the previous one is being eluted. Even so, conventional off-line SPE allows extracting more samples simultaneously.

2.2.3. Stir bar sorptive extraction

Several microextraction techniques appeared to minimize the sample volume requirements and the volume of organic solvents wasted.

One of these microextraction procedures is stir bar sorptive extraction (SBSE). SBSE could be considered an improvement of solid phase microextraction (SPME) because it has a higher volume of sorbent, providing greater sample capacity and extraction efficiency. Moreover, the stir bar device is more reusable, robust and cheaper than SPME fibres (Carpinteiro et al., 2012).

At first, only polydimethylsiloxane (PDMS) was available as a sorbent for SBSE. Later, other sorbents were developed, but the variety of options is not comparable with SPME. It is coated onto a glass-coated magnetic bar, and sampling is carried out by introducing the device into the aqueous sample. Then, the bar adsorbs the analytes that are subsequently desorbed in a lower volume of solvent (Camino-Sánchez et al., 2014). Therefore, SBSE offers efficient extraction without high solvent consumption and better preconcentration than SPME. However, given that miniaturized techniques are designed to require a lower sample volume, the obtained preconcentration factor is lower than those obtained for SPE, even in off-line mode. The SBSE procedure developed for the determination of benzotriazole derivatives in wastewater and seawater required 25 mL of sample volume and 1.5 mL of acetonitrile for desorption, so the preconcentration factor was only 16.6 (Montesdeoca-Esponda et al., 2013a).

However, the main disadvantage of SBSE is probably the long times that may be needed to reach equilibrium between the sorbent and the liquid sample, in which maximum extraction efficiencies are obtained. For benzotriazole derivatives, 120 min was required for the extraction and 20 min for the desorption, spending more than 2 h only for one sample.

Therefore, although SBSE could be preferred over off-line SPE on some occasions due to the lower sample volume required or because it can be used on-site, the preconcentration capacity and the time of extraction are serious disadvantages.

The obtained recoveries were very satisfactory for a non-exhaustive technique, ranging from 68 to 92% for almost all the analytes. For the most non-polar compound (UV-360), much lower recoveries

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were obtained (18% for seawater and 19% for wastewater). This could be due to incomplete desorption from the PDMS sorbent rather than a problem of adsorption on the stir bar. Moreover, the achieved LODs (18–55 ng·L^{-1}) are relatively high in comparison with the low concentrations of these emerging compounds in environmental samples.

2.2.4. Fabric phase sorptive extraction

Fabric phase sorptive extraction (FPSE) is one of the most revolutionary miniaturized approaches. Although it is relatively new (published in 2014) (Kabir and Furton, 2014), numerous applications have been published for the extraction of different compounds (Kabir et al., 2017; Kumar et al., 2014; Lakade et al., 2015; Locatelli et al., 2019; Racamonde et al., 2015). Similar to SBSE, FPSE is a technique that minimizes the sample volume and waste of solvent in comparison with conventional techniques such as off-line SPE.

The FPSE device is made with a sol–gel and cellulose/polyester; these improve the sorbent-analyte interaction, resulting in a better efficiency of extraction than other sorptive extraction techniques (Kumar et al., 2014). The coating is homemade, which could result in an advantage or in a drawback. The advantages are that 1) the sorbent can be prepared according to the characteristics of the target analytes and 2) the cost is low. However, not having a commercial device could be a handicap to implementing this technique in many laboratories.

For benzotriazole derivatives, two different methods using FPSE were developed, one for wastewater (Montesdeoca-Esponda et al., 2015) and the other for seawater (García-Guerra et al., 2016), because the salt content has a great influence on the selection of optimum parameters. For wastewater, only sol-gel poly(dimethyldiphenylsiloxane) (sol-gel-PDMDPS) was tested, while, for seawater, sol-gel poly(tetrahydrofuran) (sol-gel PTHF) and sol-gel poly(ethylene glycol) (sol-gel PEG) were also compared, although sol-gel PDMS was finally selected. The achieved recoveries were very different between the target analytes (more than 60% variation for wastewater and almost 40% for seawater). This limitation is due to the ability of PDMS to extract and desorb analytes being highly variable depending on their polarities.

For wastewater, 10 mL was selected as the most adequate sample volume, while 25 mL was needed for seawater. The waste of solvent was also very small, 1 mL, even less than for SBSE.

The time of extraction and desorption using FPSE for wastewater (60 and 5 min, respectively, total 65 min) was less than that for SBSE (total 140 min). However, for seawater, a very long total time (160 min) was required. This could be due to slower analyte diffusion from saline samples, which are more viscous, to the fabric. This could also explain the better recoveries obtained for wastewater (up to 99%) in comparison with those obtained for seawater (up to 46%).

However, the LODs were lower for seawater because a higher preconcentration was achieved. It must be noted that some high deviations were obtained in wastewater for some compounds (up to 29%), probably due to the interferences of the matrix.

FPSE devices are reusable and more robust than in SPME or SBSE, but their degradation must be controlled to avoid reproducibility problems.

2.2.5. Microwave assisted extraction

Unlike liquid samples, all the analytical methods developed to determine benzotriazole derivatives in solid samples from Gran Canaria Island include the use of the same extraction technique, microwave assisted extraction (MAE). The instrument was a Multiwave 6 EVAP from Anton Paar (Graz, Austria). In comparison with conventional options, such as Soxhlet or ultrasound-assisted extraction, MAE could be considered a more recent technique offering several advantages. It requires lower volumes of organic solvents than other techniques, reduces extraction time and allows the preparation of multiple samples in one single step (Esteve-Turrillas et al., 2004; Guedes-Alonso et al., 2016; Llompart et al., 2019).

If the analysis of liquid environmental samples is often complicated, the determination in solid samples is even more complex. Strong solute-matrix interactions can be difficult to disrupt. Therefore, the powerful microwave energy to break these interactions could be an important tool in an analytical laboratory.

To obtain the maximum extraction efficiencies, several parameters must be optimized in an MAE procedure depending on the characteristics of the matrix, namely, sample amount, kind of solvent, solvent volume, power and time. The optimum parameters for the extraction of target benzotriazole derivatives from sludges (Montesdeoca-Esponda et al., 2013b), marine sediments (Montesdeoca-Esponda et al., 2013b), seaweed (Pacheco-Juárez et al., 2019) and fish (Montesdeoca-Esponda et al., 2020) are compared in Table 2.

The first major difference among the MAE conditions employed for target compounds in each matrix is the sample amount. For sludges and marine sediments (matrices that usually do not present problems to be sampled), 1 g was employed to maximize the responses. However, for seaweed and fish samples, which were more

Table 2
Comparison of the MAE-UHPLC-MS/MS methods used for the determination of benzotriazole derivatives in solid samples.

Matrix		Sample amount (g)	Power (W)	Time (min)	Solvent	Extractant volume (mL)	Extraction efficiency (%)	Precision (RSD, %)	LODs (ng·g $^{-1}$)	LOQs (ng·g $^{-1}$)	Ref.
Sludge		1	300	5	Acetonitrile	2	46.1–82.4	8.57–16.3	0.07–0.15	0.23–0,50	Montesdeoca-Esponda et al., 2013b
Sediment							50.1-87.1	8.16–13.6	0.05–0.11	0.17–0,37	
Seaweed		0.1	500	5	Methanol	2.5	49.8–92.3	3.44–8.52	0.89–1.76 (dw) [a]	2.97–5,87 (dw)	Pacheco-Juárez et al., 2019
Fish	Muscle	0.1	300	10	Acetonitrile	2.5	13.1–75.4	0.21–6.06	0.34–2.87 (dw)	1.13–9,57 (dw)	Montesdeoca-Esponda et al., 2020
	Viscera						22.9–72.8	0.32–5.26	0.60–2.43 (dw)	2.00–8,10 (dw)	

[a] dw: dry weight.

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difficult to obtain in high amounts, 0.1 g was sufficient to develop the MAE procedure.

The applied power ranged from 300 to 500 W, being adequate to liberate the analytes from the solid matrix towards the solvent, but not so high to damage the sample, which could generate interferences in the determination. The highest power was required for seaweed samples, probably due to the strong interaction between the analytes and the vegetal matrix.

The optimum extraction time also varies among the matrices, but short periods were always required (between 5 and 10 min). The complete procedure includes 10 min to cool down and at least a filtration of the extract before the injection in the detection system, so each extraction normally requires approximately 30 min. The consumed organic solvent (2–2.5 mL) is also lower than in conventional techniques for solid matrices.

For the determination of benzotriazole derivatives in sludge and marine sediment, a cleaning step based on SPE (on-line mode) was implemented (Montesdeoca-Esponda et al., 2013b). This provided a purified and more concentrated extract, reaching LODs in the range 0.07–0.15 ng·g^{-1} for sludges and even lower, between 0.05 and 0.11 ng·g^{-1}, for sediments. MAE is a very robust technique; however, although on-line SPE also provides good reproducibility of the replicates, the multiple steps required in this analytical procedure caused some relatively high deviations (between 7.8 and 15.5% for sludges and from 8.83 to 16.3% for sediments). The obtained recoveries, in the ranges of 46.1–82.4% for sludges and 50.1–87.1% for sediments, were better for the less non-polar compounds and lower for the most non-polar compounds.

Better intraday precision was obtained for seaweed samples, between 3.44 and 8.52%. However, some outstanding values were registered for interday precision for some compounds (e.g. 21.9 and 9.20% for UV-329 at 100 and 400 ng·g^{-1}, respectively). In this case, clean-up and preconcentration steps were not employed. Most likely, and due to the matrix effect of such a complex vegetal matrix, the achieved LODs were one order of magnitude higher than those for sludges and marine sediments (between 0.89 and 1.76 ng·g^{-1}, expressed in dry weight (dw)) (Pacheco-Juárez et al., 2019). A subsequent SPE step (on-line or off-line mode) or evaporation of the extract and its redissolution in a lower volume of solvent could be implemented to improve the sensitivity of the method.

LODs on this order of magnitude were also obtained in the determination of benzotriazole derivatives in fish samples in the ranges 0.34–2.87 ng·g^{-1} (dw) for muscle and 0.60–2.43 ng·g^{-1} (dw) for viscera (Montesdeoca-Esponda et al., 2020). The obtained recoveries for some compounds in this kind of sample were significantly worse than those for sediments, sludges and seaweed. In this case, the lowest efficiencies were measured for the less non-polar compounds to be as low as 13.1 and 22.9% for UV-P in muscle and viscera, respectively. In contrast, the most non-polar compound, UV-360, which was poorly extracted from other matrices, presented recoveries between 60.3 and 75.4% from fish samples.

2.3. Determination

Despite the application of the extraction techniques described before, which provide purified and more concentrated extracts, the analysis of target micropollutants in such complex matrices requires powerful analytical equipment to obtain adequate sensitivity and selectivity.

Although several works employed gas chromatography (GC) for the separation and identification of these compounds (Carpinteiro et al., 2012, 2010; Kameda et al., 2011; Liu et al., 2012, 2011; Nakata et al., 2009), liquid chromatography (LC) is the most commonly employed technique in the analysis of environmental samples because it is useful for volatile and non-volatile compounds (Kim et al., 2011a, 2011b; Liu et al., 2014; Peng et al., 2015; Ruan et al., 2012; Song et al., 2014). Normally, these systems are coupled with mass spectrometry detectors, which provide the selectivity and sensitivity required for the analysis of these analytes in such samples.

In this way, ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS) was used for the determination of target benzotriazole derivatives in samples from Gran Canaria Island.

The equipment employed was an ACQUITY UHPLC (Waters Chromatography, Barcelona, Spain) with a triple quadrupole mass spectrometry detector (TQD) and an electrospray interface (ESI). The specific detection parameters applied for each compound are shown in the supplementary material (Table SM1). For chromatographic separation, an ACQUITY UHPLC Waters BEH C$_{18}$ column (50 mm × 2.1 mm and 1.7 μm particle size) was used at 35 °C. The mobile phase consisted of methanol with 0.1% formic acid in isocratic mode.

Quality control was assessed for each developed method by calculation of extraction efficiencies, linearity, precision and limits of detection/quantification. Tables 1 and 2 summarize the achieved analytical parameters for liquid and solid matrices, respectively.

To overcome the matrix effect, calibration curves were built using the matrix match calibration approach (García-Guerra et al., 2016; Montesdeoca-Esponda et al., 2020; Montesdeoca-Esponda et al., 2015, 2013a, 2013b; Pacheco-Juárez et al., 2019), except for SPE-UHPLC-MS/MS methods, for which the standard additions method was applied (Montesdeoca-Esponda et al., 2012). Good linearity was obtained in all cases, with linear correlation coefficients higher than 0.992.

Extraction efficiencies were tested for at least two concentrations for each studied matrix in three replicate samples. For waters extracted using on-line SPE (Montesdeoca-Esponda et al., 2012) and for sediments and sludges treated with MAE (Montesdeoca-Esponda et al., 2013b), three concentration levels were tested.

Different concentration levels were also employed to evaluate precision, expressed as the relative standard deviation (RSD), using six replicate samples. In the works involving FPSE (García-Guerra et al., 2016; Montesdeoca-Esponda et al., 2015), as well as in the analysis of seaweeds (Pacheco-Juárez et al., 2019) and fish (Montesdeoca-Esponda et al., 2020), not only intraday but also interday precisions were evaluated.

LODs and LOQs were obtained from the signal-to-noise ratio (S/N) for the analyte peaks, assuming minimum detectable S/N levels of 3 and 10, respectively.

3. Occurrence in environmental samples from Gran Canaria (Spain)

The previously described analytical methods were applied to determine the six target benzotriazole derivatives in different kinds of samples taken around Gran Canaria Island (Fig. 3):

I. Wastewaters taken in 8 WWTPs with different treatments
II. Sludges from 3 of these WWTPs
III. Seawater from 2 different ecosystems: beaches and marine outfalls surroundings
IV. Sediments also from beaches and marine outfalls surroundings
V. Seaweeds (13 species)
VI. Fish (3 species)

Moreover, in the works analysing these samples, two different approaches were carried out. Some of the studied samples were taken at a single time, so they provide information only about the situation

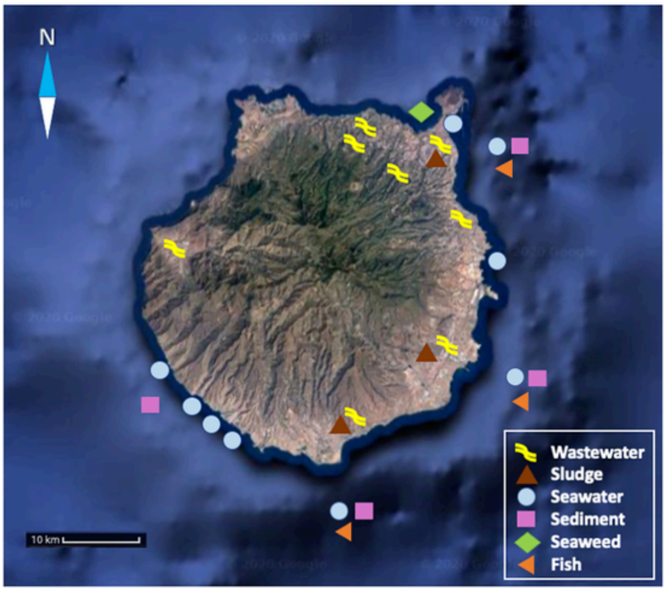

Fig. 3. Location of the samplings for the determination of benzotriazole derivatives in Gran Canaria island (developed from Google Maps).

of a certain location at a specific moment. In contrast, other samples belong to a 2-year monitoring programme, from which some temporal and spatial variations could be observed.

In the next sections, the results obtained for the analysis of target analytes in samples from Gran Canaria Island using those approaches will be reviewed. The frequency of detection of target compounds in every matrix is presented in Fig. 4, in which different accumulation trends can be observed in each matrix. Moreover, Table 4 summarizes the range of concentrations measured for each compound in the different matrices and offers a comparison with other studies.

3.1. Wastewaters

Since the major sources of emerging compounds in the oceans are WWTP effluents, their monitoring is essential to determine the fate of these pollutants. Different studies have been carried out to determine benzotriazole derivatives in wastewaters from Gran Canaria Island.

The effluents from seven different conventional WWTPs were analysed in 2012 using on-line SPE followed by UHPLC-MS/MS (Montesdeoca-Esponda et al., 2012). Their location and detailed characteristics are summarized in Table 3. All of these WWTPs had activated sludge as a secondary treatment, except one that used a membrane bioreactor. Two of them also applied tertiary systems based on microfiltration and reverse osmosis. Six target analytes were found, but their presence in the different WWTPs was not homogeneous. They were found in six of the seven analysed samples, in which a minimum of two compounds were measured, with UV-P and UV-328 being the most frequently detected (in 57.1 and 71.4% of the samples, respectively). In three WWTPs, up to three different benzotriazole derivatives were measured (UV-P, UV-328 and UV-360 in two of them and UV-326, UV-328 and UV-360 in the other). UV-P, UV-326 and UV-327 were measured only in one WWTP, while UV-360 was found in two of them. No relation between the mechanism of depuration applied and the occurrence of target analytes was observed.

Relatively low concentrations were measured. The maximum reported concentrations were UV-P, 8.8 ng·L^{-1}; UV-326, 11 ng·L^{-1}; UV-327, 4.8 ng·L^{-1}; UV-328, 13 ng·L^{-1}; UV 329, 4.0 ng·L^{-1}; and UV-360, 6.6 ng L^{-1}.

However, the posterior application of SBSE-UHPLC-MS/MS to the effluents from three of these WWTPs (the three largest ones) did not reveal the presence of benzotriazole derivatives (Montesdeoca-Esponda et al., 2013a). The selected systems in this case were i) secondary treatment with membrane bioreaction, ii) secondary treatment with activated sludge and iii) tertiary treatment with reverse osmosis, which were applied for locations in the north, south and east of the island, respectively. Given that the LODs provided by this methodology were higher than the concentrations previously found using on-line SPE-UHPLC-MS/MS, the lack of positive results is probably because the sensitivity of the SBSE-UHPLC-MS/MS method was not high enough to detect the analytes at the required levels.

Conversely, using another miniaturized extraction procedure, FPSE, two target compounds were detected in the effluents of the same three WWTPs mentioned before (Montesdeoca-Esponda et al., 2015). UV-328 was measured between 17.0 and 60.5 ng·mL^{-1}, and UV-360 was measured in the range from 69.3 to 99.2 ng·mL^{-1}. The highest concentrations were found in the WWTP in which only secondary treatment was conducted.

After these previous studies, in which single-time samples were analysed, - monitoring was carried out between 2016 and 2018 to compare the presence of benzotriazole derivatives in several WWTPs of Gran Canaria Island at different times (Montesdeoca-Esponda et al., 2019). In this case, five WWTPs, four conventional and one employing a natural depuration system, were selected to analyse not only effluents as in the previous studies but also influents, which allowed determination of the removal efficiency of target analytes during the treatment. The characteristics of the selected conventional WWTPs were very different and were designed to treat wastewater from 6000 to 600,000 equivalent inhabitants. Two of them only possessed secondary treatment, while the others also applied tertiary treatment. Moreover, in one of them, the effluents of two different tertiary treatments were evaluated: microfiltration and reverse osmosis. Finally, a smaller natural depuration system based on gravel and plants was included in the study. This natural WWTP treats only the waters from a part of a university campus on Gran Canaria Island. The samples were taken quarterly for two years, resulting in a wide monitoring of 88 wastewater samples.

In conventional WWTPs, some of the target analytes were found in 20.5% of the samples, appearing in all locations at concentrations between 13.12 and 1933 ng·L^{-1}. The most frequently measured compound was UV-329, which appeared in 33% of the influent samples (in the range 106–1933 ng·L^{-1}) and in 10% of the effluent samples (in the range 49.54–570.9 ng·L^{-1}). UV-328 and UV-360 were also detected but at much lower frequencies (around 3%).

Although the concentrations measured in the influents were usually higher than in effluents, the remaining residues demonstrated that target analytes suffer incomplete elimination in the WWTPs. Given the low solubility and high log K_{ow} of analytes, the achieved removal is probably due to their adsorption in the suspended solids.

The major number of different benzotriazole derivatives found corresponded to the WWTPs located in the south of the island, which receive wastewater from a multitude of hotels and touristic flats.

Although the highest frequency of detection was observed in the smaller WWTPs, the results normalized according to the volume of treated water and the equivalent population showed that the concentrations were similar for all the studied WWTPs.

Finally, target compounds were not detected in the samples from the natural depuration system, neither in effluent nor in influent (Guedes-Alonso et al., 2020). This is probably because PCPs are normally used at home, so the wastewaters from a university campus do not usually contain UV filters and stabilizer compounds, or their

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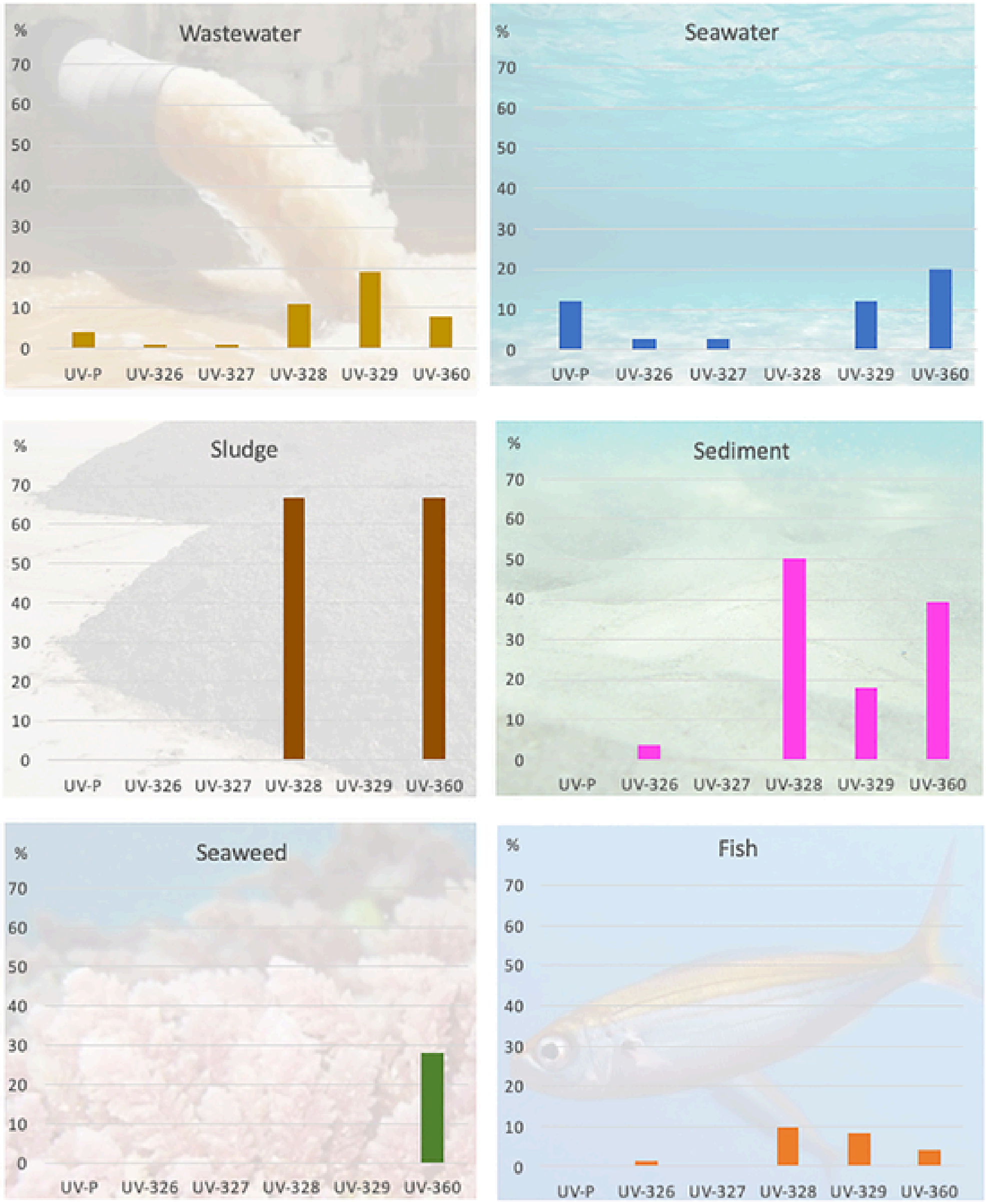

Fig. 4. Frequency of detection of target compounds in each matrix analysed in Gran Canaria island.

Table 3
Characteristics of studied conventional WWTPs (information obtained from iAgua Data, https://www.iagua.es/data/infraestructuras/edar/comunidad/canarias-111).

Location (Gran Canaria)	Treatment applied	Inlet flow (e.i.)	Design population (e.i.)
N	Activated sludge	25,247	20,000
N	Membrane bioreactor	4457	6000
NE	Activated sludge	200,749	600,000
NE	Activated sludge	42,335	50,000
E	Activated sludge and reverse osmosis	134,000	150,000
S	Activated sludge	12,500	100,000
W	Activated sludge	7372	10,000

e.i.: equivalent inhabitant.

concentrations are lower than the LODs of the employed analytical method.

In general, the range of detected concentrations in wastewater samples, from tens to hundreds of ng L^{-1}, is in agreement with those reported in the literature (in the range 2–414 ng L^{-1} for influents and 6–55 ng L^{-1} for effluents) (Carpinteiro et al., 2010; Kameda et al., 2011; Krzeminski et al., 2017; Liu et al., 2014, 2012; Song et al., 2014). However, the levels measured for UV-329 in influent samples from Gran Canaria Island (up to 1933 ng L^{-1}) stand out over the values registered in other worldwide locations, almost five times higher than the maximum concentrations reported by Liu et al. (2012). All the mentioned works also employed powerful detection systems (MS/MS) coupled to liquid or gas chromatography, normally after the application of conventional or on-line SPE.

3.2. Seawater

As also occurred for wastewaters, different approaches have been employed for the analysis of target compounds in seawater from

Table 4
Comparison of the occurrence of benzotriazole UV filters and stabilizers in environmental matrices of Gran Canaria island and other studies. Range of concentrations expressed in ng L $^{-1}$ for liquid samples and in ng g $^{-1}$ (dw) for solid samples.

			This study	Other studies			
Wastewaters	Influent	UV-P	n.d.	9.9–37.1 (Liu et al., 2014)	13.2–50.3 (Song et al., 2014)	5–16 (Carpinteiro et al., 2010)	
		UV-326	n.d.	n.d. (Liu et al., 2014)	10.6 (Song et al., 2014)	26–40 (Carpinteiro et al., 2012)	15–35 (Liu et al., 2012)
		UV-327	n.d.	Up to 10 (Langford et al., 2015)	n.d. (Liu et al., 2014)	22–85 (Carpinteiro et al., 2012)	n.d. (Carpinteiro et al., 2010)
		UV-328	22.55–238	Up to 5 (Langford et al., 2015)	2.6–2.9 (Liu et al., 2014)	9.90 (Song et al., 2014)	53–76 (Carpinteiro et al., 2012)
		UV-329	106–1933	2–16 (Krzeminski et al., 2017)	Up to 5 (Langford et al., 2015)	3.8 (Liu et al., 2014)	227–414 (Liu et al., 2012)
		UV-360	13.1–68.4				
	Effluent	UV-P	4.9–8.8	7.1–15.9 (Liu et al., 2014)	10.6 (Song et al., 2014)		
		UV-326	11	n.d. (Liu et al., 2014)	n.d. (Song et al., 2014)	n.d. (Carpinteiro et al., 2012)	55 (Liu et al., 2012)
		UV-327	4.8	n.d. (Liu et al., 2014)	31 (Carpinteiro et al., 2012)		
		UV-328	0.017–13	n.d.–0.6 (Liu et al., 2014)	2.74 (Song et al., 2014)	21 (Carpinteiro et al., 2012)	
		UV-329	49.54–57.09	6–11 (Krzeminski et al., 2017)	n.d. (Liu et al., 2014)	98 (Liu et al., 2012)	n.d. (Liu et al., 2011)
		UV-360	0.069-6.6				
Seawater		UV-P	2.8–141.4	n.d. (Tashiro and Kameda, 2013)			
		UV-326	1642–2419	0.1–3.6 (Tashiro and Kameda, 2013)			
		UV-327	168.2–893.0	0.1–0.3 (Tashiro and Kameda, 2013)			
		UV-328	n.d.	2.8–287 (Tashiro and Kameda, 2013)			
		UV-329	67.5–859	n.d. (Tashiro and Kameda, 2013)			

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			This study	Other studies			
		UV-360	3.6–544.9				
Sludges		UV-P	n.d.	0.96–96.4 (Ruan et al., 2012)	n.d. (Kameda et al., 2011)		
		UV-326	n.d.	48–114 (Liu et al., 2012)	4–3390 (Ruan et al., 2012)	49.9 (Liu et al., 2011)	0.4–5.4 (Kameda et al., 2011)
		UV-327	n.d.	30.4–159.9 (Langford et al., 2015)	1.53–25.5 (Ruan et al., 2012)	0.3–1.0 (Kameda et al., 2011)	
		UV-328	0.94–12.2	Up to 25 (Langford et al., 2015)	3.54–2470 (Ruan et al., 2012)	10–85 (Kameda et al., 2011)	
		UV-329	n.d.	1172–3303 (Langford et al., 2015)	27–272 (Liu et al., 2012)	0.57–757 (Ruan et al., 2012)	122.9 (Liu et al., 2011)
		UV-360	2.30–6.32				
Marine sediments		UV-P	n.d.	0.10–0.24 (Apel et al., 2018a)	0.02–0.06 (Apel et al., 2018b)	0.61–1.83 (Peng et al., 2017)	
		UV-326	93.46	0.13–0.97 (Apel et al., 2018a)	0.65–1.96 (Apel et al., 2018b)	0.46–9.00 (Peng et al., 2017)	1.5–12 (Nakata et al., 2009)
		UV-327	n.d.	0.16–0.24 (Apel et al., 2018a)	0.50–1.23 (Apel et al., 2018b)	0.2–93 (Peng et al., 2017)	Up to 8.1 (Langford et al., 2015)
		UV-328	0.347–24.0	0.07–0.88 (Apel et al., 2018a)	0.12–0.41 (Apel et al., 2018b)	0.4–3.2 (Peng et al., 2017)	3.2–25.1 (Langford et al., 2015)
		UV-329	0.004–2.162	Up to 0.23 (Apel et al., 2018a)	0.04–6.09 (Apel et al., 2018b)	0.048–0.830 (Peng et al., 2017)	n.d. (Langford et al., 2015)
		UV-360	0.18–1.862	0.21–4 (Apel et al., 2018a)			
Seaweeds		UV-P	n.d.				
		UV-326	n.d.				
		UV-327	n.d.				
		UV-328	n.d.				
		UV-329	n.d.				
		UV-360	42.5–115				
Marine fish	Muscle	UV-P	n.d.	0.40 (Peng et al., 2015)	0.03–0.41 (Kim et al., 2011a)	0.06–0.21 (Kim et al., 2011b)	
		UV-326	9.69–34.9	7.95 (Peng et al., 2015)	0.02–0.49 (Kim et al., 2011a)	0.14–0.48 (Kim et al., 2011b)	< 0.1–5.6 (Nakata et al., 2009)
		UV-327	n.d.	1 (Peng et al., 2015)	0.004–0.54 (Kim et al., 2011a)	0.006–0.13 (Kim et al., 2011b)	< 0.12–13 (Nakata et al., 2009)
		UV-328	4.16–29.8	n.d. (Peng et al., 2015)	0.03–0.56 (Kim et al., 2011a)	0.001–0.03 (Kim et al., 2011b)	< 0.15–55 (Nakata et al., 2009)
		UV-329	n.d.	0.11 (Peng et al., 2015)	0.005–0.52 (Kim et al., 2011a)	0.04–0.06 (Kim et al., 2011b)	

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			This study	Other studies
		UV-360	5.20–7.19	
	Viscera	UV-P	n.d.	0.67 (Peng et al., 2015)
		UV-326	n.d.	11.4 (Peng et al., 2015)
		UV-327	n.d.	1.8 (Peng et al., 2015)
		UV-328	2.99–45.6	0.8 (Peng et al., 2015)
		UV-329	1.34–10.7	n.d. (Peng et al., 2015)
		UV-360	4.46–34.5	

n.d.: not detected.

Gran Canaria Island. For the analysis using on-line SPE, six beaches were sampled, each at two different points. Two of them are in the north (Alcaravaneras) and east of the island (Melenara), visited mainly in summer by local people, while the others are in the south (Anfi del Mar, Puerto Rico, Amadores and Mogán), which is the most touristic area with visitors all the year. Two benzotriazole derivatives, UV-P and UV-360, were found in concentration ranges of 2.8–4.4 and 3.6–5.2 ng·L^{-1}, respectively. All positive results were found in the most visited beaches in the south of the island (15.4% in Anfi del Mar, 23.0% in Puerto Rico, 30.8% in Amadores and 30.8% in Mogán).

Three of these very touristic beaches (Puerto Rico, Amadores and Mogán) were later selected to apply a SBSE-UHPLC-MS/MS method. Nevertheless, with the sensitivity provided by this procedure, no compounds were detected (Montesdeoca-Esponda et al., 2013a).

However, UV-360 was detected in seawater from the same three beaches using FPSE-UHPLC-MS/MS in the range from 41.12 to 544.9 ng·L^{-1} (García-Guerra et al., 2016). Four samples were taken in each one before and after Easter to compare the influence of holidays in the presence of this kind of compound. A total of 24 samples were analysed, and UV-360 was found in nine of the sampling points. Although this compound was detected at all the studied beaches, no significant differences were observed between the concentrations registered before and after the Easter holidays. Most likely, this effect could be seen clearer in beaches mainly visited by local people, since foreign tourism is more or less homogeneous throughout the year.

Following the monitoring approach described for wastewater, the marine discharges of the previously described WWTPs, applying 1) secondary treatment with membrane bioreaction, 2) secondary treatment with activated sludges and 3) tertiary treatment with reverse osmosis, were selected to study the occurrence of benzotriazole derivatives once released to the sea. Therefore, seawater close to marine outfalls corresponding to the main WWTPs in the north, east and south of the island were also analysed for two years (July 2016–July 2018). At each point, deep and superficial seawater samples were taken, and benzotriazole derivatives were detected in both, despite the dilution suffered by superficial seawater samples (Montesdeoca-Esponda et al., 2019).

As in wastewater samples, UV-329 was the most frequently detected compound in seawater (in 19% of the samples), being measured in the range 67.5–859.0 ng·L^{-1} in all the studied locations. Likewise, the detection of target analytes was prominent in the marine outfall corresponding to the WWTP of the most touristic area of the island (the south) but at a lower frequency than in wastewaters. Additionally, at some sampling points, target analytes appeared in superficial but not in deep samples. This could come from the use of sunscreens in nearby beaches more than from wastewater discharges.

UV-P, UV-326 and UV-327 were also found in seawater samples close to marine outfalls. However, more occasionally, they did not show a spatial trend. No temporal differences were observed for seawater samples either.

To the best of our knowledge, these compounds are not frequently monitored in seawater samples. The concentrations measured in Gran Canaria were compared with those reported by Tashiro and Kameda (2013) on the touristic island of Okinawa (Japan); surprisingly, UV-P and UV-329 were not found, while, on Gran Canaria Island, they were measured at relatively high concentrations (141 and 859 ng L^{-1}, respectively). The maximum concentrations of UV-326 and UV-327 were also much higher in Gran Canaria than in Okinawa (2419 vs 3.6 and 893 vs 0.3 ng L^{-1}, respectively). In contrast, these authors using GC–MS found concentrations up to 287 ng L^{-1} for UV-328, which was not detected in Gran Canaria. These disparities could demonstrate the different uses of sunscreen ingredients in various countries.

3.3. Sludges

The determination of benzotriazole derivatives in sludges from Gran Canaria Island has only been conducted in single-time samples. Samples obtained in 2013 from three WWTPs were analysed using MAE with on-line SPE as a clean-up step followed by UHPLC-MS/MS (Montesdeoca-Esponda et al., 2013b). Due to the high hydrophobicity of most of the target analytes, these samples, coming from the activated sludge treatment, could be an interesting matrix in which to understand the elimination of these pollutants in the WWTPs. Two of the selected systems applied activated sludge, and the other had a membrane bioreactor treatment, in which the production of sludge was lower.

Two compounds were found in the analysed sludges. UV-328 was measured in two WWTPs, one with activated sludge followed by reverse osmosis and the other with a membrane bioreactor, at concentrations of 0.94 ng·g^{-1} and 12.2 ng·g^{-1}, respectively. UV-360 was also found in two of the three sampled WWTPs. The measured concentrations were 2.30 ng·g^{-1} in the WWTP with activated sludge and

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6.32 ng·g^{-1} in the WWTP with a membrane bioreactor. Although no significant differences were observed regarding the applied treatment, it seems that sludges from the WWTP with the membrane bioreactor accumulated higher concentrations of target analytes.

Other benzotriazoles (UV-P, UV-326, UV-327 and UV-329) were measured in higher concentrations in sludge samples in other countries, such as China (Ruan et al., 2012), Japan (Liu et al., 2011, 2012) and Norway (Langford et al., 2015). Ruan et al. (2012) carried out a wide study of 60 WWTPs from 33 cities in China and found concentrations as high as 3390 ng g^{-1} for UV-326. Langford et al. (2015) measured almost the same concentration level (3303 ng g^{-1}) for UV-329. All these analyses were conducted using MS/MS detection.

Since only three single-time samples were analysed in the study carried out in Gran Canaria, larger monitoring programmes are required to obtain reliable conclusions about the presence of these compounds in sludge.

3.4. Marine sediments

MAE and on-line SPE followed by the UHPLC-MS/MS procedure were used to determine target benzotriazole derivatives in marine sediments of different places and characteristics from Gran Canaria Island.

First, it was applied to analyse sediments from three touristic beaches on the south side of the island (Puerto Rico, Amadores and Mogán). The samples taken in the shoreline did not reveal the presence of target compounds (Montesdeoca-Esponda et al., 2013b).

In the same work from 2013, sediments located in an area influenced by a marine outfall were taken. The outfall is located in the southwest region of Gran Canaria Island and corresponds to a small WWTP designed to purify the wastewaters of some hotels. Since the discharge of the depurated waters is situated several km offshore in front of the beach (Taurito Beach), four equidistant points were selected between outfall and beach to collect the samples. Two compounds, UV-328 and UV-360, were found at the three sampling points closest to marine outfall, in concentrations in the ranges of 20.7–24.0 ng·g^{-1} and 0.18–0.33 ng·g^{-1}, respectively. These were highest at the points closest to the discharge and lowest at the furthest. At the point closest to the beach, no compounds were detected, which could be explained by the dilution of the waters discharged by the outfall.

Finally, the target compounds were monitored for two years in marine outfalls from the north, east and south of the island within the monitoring programme described previously for seawater. Quarterly samples from July 2016 to July 2018 were taken from the bottom of the sea in the area close to the discharge (Montesdeoca-Esponda et al., 2019).

Four of the six target compounds were found in these marine sediments (UV-326, UV-328, UV-329 and UV-360). The most detected were UV-328 and UV-360, the most non-polar compounds, in 46 and 33% of the samples, respectively. The measured concentrations ranged from 347.2 to 1788 ng·kg^{-1} (dw) for UV-328 and from 546.9 to 1862 ng·kg^{-1} (dw) for UV-360. Although the concentrations of UV-360 were higher, UV-328 was found in all studied locations, while UV-360 was detected in only two of them. As for seawater samples, the most prominent pollution due this kind of compound was observed in the south, where most tourism facilities of the island are located.

These concentration levels are higher than those found by Apel et al. in sediments of the European North and Baltic Seas (Apel et al., 2018a) and the Chinese Bohai and Yellow Seas (Apel et al., 2018b), where maximum values of 4 and 6 ng·g^{-1}, respectively, were reported. Levels relatively higher were found in sediments in China (Peng et al., 2017) and Norway (Langford et al., 2015), with maximum values of 93 ng·g^{-1} for UV-327 and 25 ng·g^{-1} for UV-328. The determination of the analytes was carried out using LC-MS/MS in all these works.

3.5. Seaweeds

Sessile organisms such as seaweeds could be able to accumulate micropollutants present in the surrounding water. They have already been used as bioindicators of contamination in the environment (e.g. for metals and organic compounds (Bonanno et al., 2020; Chakraborty et al., 2014; Komar et al., 2018; Lourenço et al., 2019)).

A first approach to determine the presence of benzotriazole derivatives in biota from Gran Canaria Island was carried out by analysing seaweed samples taken in Las Canteras, a very crowded beach situated in the capital, Las Palmas de Gran Canaria. A MAE-UHPLC-MS/MS procedure was applied to twelve seaweed species (ten of the phylum Ochrophyta, one Rhodophyta and one Chlorophyta). In this case, the temporalization of the samplings depended on the reach of seaweeds to the beach because only those organisms that the tide had left on the shore were picked up. The study was accomplished between March and June 2018 (Pacheco-Juárez et al., 2019).

Only UV-360, the most non-polar compound among the target analytes, was found in five species: *Asparagopsis taxiformis*, *Halopteris filicina*, *Padina pavonica*, *Sporochonus pedunculatus* and *Lobophora variegata*.

It was detected only in the samples collected in May and June, which could be due to a higher number of visitors in the beach during these months. UV-360 is one of the compounds allowed in Europe to be used as a UV filter in cosmetics (European Parliament and of the Council, 2009), so it is commonly found in sunscreen formulations. The measured concentrations of this compound were between 42.5 and 115 ng·g^{-1} (dw). Although it was measured more frequently in Ochrophytas, the highest values were measured in the species *Asparagopsis taxiformis*, a Rhodophyta. No analyte was found in Chlorophyta *Cymopolia barbata*, although it was sampled in all studied months.

The measured concentrations for the Rhodophyta *Asparagopsis taxiformis* were similar in May and June, while for the Ochrophytas, they were slightly higher in June than in May.

To our knowledge, other studies regarding the presence of these compounds in seaweed samples have not been conducted.

3.6. Fish

Most works studying the negative effects of UV filters and stabilizers in living organisms are focused on fish samples, probably because they are important path of transmission to humans through the trophic chain. This is the last matrix in which benzotriazole derivatives were analysed in Gran Canaria.

Wild fish samples were collected near the same marine outfalls monitored for the seawater and marine sediment studies and were analysed quarterly for two years between 2016 and 2018. In each of the three selected marine outfalls, three common species of fish that normally visit these areas for feeding were selected: *Sphoeroides marmoratus*, *Sphyraena viridensis* and *Boops boops*. Muscle and viscera were analysed separately (Montesdeoca-Esponda et al., 2020), which means that a large study of 144 samples was carried out.

In muscle samples, three target compounds, UV-326, UV 328 and UV 360, were detected in concentrations from 4.16 ng·g^{-1} to 34.9 ng·g^{-1} (dw). The proportion of analysed samples that presented benzotriazole derivatives in the muscle was significant, 18.1%. The

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compound most frequently detected was UV-328, which was found in the three studied species (between 4.16 and 29.8 ng g^{-1}). UV-326 was found in two species (*S. marmoratus* and *B. boops*), while UV-360 was measured only in *B. boops*.

Therefore, more target analytes were detected in *B. boops*. Moreover, the maximum concentrations for each analyte were found in this species: 34.9 ng·g^{-1} (dw) for UV-326, 29.8 ng·g^{-1} (dw) for UV-328 and 7.19 ng·g^{-1} (dw) for UV-360. This is probably because this fish is omnivorous, so it could incorporate these pollutants by bioaccumulation.

A higher frequency of detection was observed in viscera samples (in 26.4% of the samples), in which UV-328, UV-329 and UV-360 were found. Despite some outstanding concentrations (e.g. 45.6 ng g^{-1} (dw) for UV-328 in *B. boops*), the obtained levels were generally low (below 10 ng·g^{-1}).

UV-329 was the compound that appeared on most occasions in viscera in 8.3% of the analysed samples. It was present in all the studied locations and species at concentrations ranging from 1.34 to 10.7 ng·g^{-1}.

The marine outfall in San Agustín, in the south of the island, showed a large number of positives (46.9%), but no clear trend of temporal or spatial variability was obtained.

There are few studies regarding the presence of these compounds in marine fish species, and most of them have been conducted in muscle. In this matrix, concentrations lower than those found in Gran Canaria (up to 1 ng g^{-1}) normally have been reported in China (Peng et al., 2015) and the Philippines (Kim et al., 2011a, 2011b). However, these works reported the presence of UV-P, UV-327 and UV-329, which were not found in the samples from Gran Canaria island. Only Nakata et al. (2009) measured higher concentrations (up to 55 ng $g^{-1)}$ in fish species from Japan. In viscera samples, some compounds not found in Gran Canaria species were reported in China (UV-P, UV-326 and UV-327) (Peng et al., 2015), while compounds measured at concentrations up to 10.7 (UV-329) and 45.6 ng g^{-1} (UV-328) in Gran Canaria were not detected (or were detected at extremely low concentrations) in China. All these authors employed LC-MS for the analysis, except Nakata et al. (2009) used GC–MS.

4. Conclusions and future trends

The increasing release of chemical compounds to the environment necessitates an evaluation of their fate and mobility. To include hazardous compounds of wide use, such as UV filters and stabilizers, in future European water framework directives, it is essential to determine their presence in as many matrices and locations as possible. The exhaustive study and deep characterization of small places such as Gran Canaria Island could be helpful to understand the behaviour and distribution of pollutants in similar areas. The results could even be used to extrapolate the observations to a larger scale.

Given the special characteristics of some UV filters and stabilizers and the complexity of the environmental samples, the development of selective and sensitive determination methodologies is a key factor in achieving this goal. The revision of different approaches to analyse benzotriazole derivatives in very varied matrices demonstrates that the selection of an adequate procedure is essential to achieve suitable analytical parameters for each matrix requirement.

Microextraction techniques, such as SBSE or FPSE, offer advantages including minimized waste of sample and solvents or the possibility to use them on-site. However, their relatively high LODs in comparison with other conventional techniques such as SPE could involve analytes in very low concentrations that are sometimes undetected.

Other approaches, such as automatization (e.g. on-line SPE), are an alternative to minimize the volumes of sample and solvents and to diminish handling, promoting better reproducibility. Nevertheless, the cost of the instrumentation, the availability of consumables (e.g. variety of sorbents) or the required time per sample could also be important points to take into account for the implementation of a methodology in a chemical laboratory.

The application of different analytical methods to the determination of benzotriazole derivatives in samples from Gran Canaria Island (Spain) allowed demonstration of their presence in different kinds of environmental matrices. The most ubiquitous was UV-360, which was measured in all the samples, with its detection frequency being higher in solid samples. This is probably because this compound is the most non-polar among the selected analytes.

In addition to UV-360, the detection frequency of UV-328, the second most non-polar compound, stands out in sludge and marine sediments. The affinity of these compounds for this kind of matrix raises the challenge of a deeper study for both of them. Only three single-time samples of sludge were obtained in the reviewed works, so a wider study is necessary to understand the adsorption of target compounds in this matrix as a mechanism of the elimination in WWTPs. On the other hand, the study of suspended particles in addition to sediments from the bottom could help to determine the removal of benzotriazole derivatives from the water column in the ocean.

The samples that were polluted with a higher number of compounds were wastewaters and seawater. The six target compounds were found in wastewaters, while seawater contained five of them. However, the frequency of detection in these matrices was less than 20% in all cases, much lower than for marine sediments or sludges. The variety of detected compounds in these matrices could reveal that pollutants reach the environment through direct or indirect discharges and are then transported to other compartments, such as marine sediments or organisms.

Finally, regarding biota samples, significant frequencies of detection were reported for some compounds (e.g. almost 30% for UV-360) in seaweed. In fish samples, the detection of this compound was relatively low, but four other target compounds were detected (UV-P, UV-326, UV-327 and UV-329).

The reviewed works also revealed that samples taken in the most touristic part of Gran Canaria Island showed the highest pollution by the target compounds, which could confirm that this economic activity has a significant influence on the environment. Therefore, future studies are necessary to evaluate the risk of these compounds to marine ecosystems and to human health since they can suffer bioaccumulation and biomagnification in the trophic chain.

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CRediT authorship contribution statement

Sarah Montesdeoca-Esponda: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **María Esther Torres-Padrón:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – review & editing. **Zoraida Sosa-Ferrera:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **José Juan Santana-Rodríguez:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

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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