



Occurrence and environmental hazard of organic UV filters in seawater and wastewater from Gran Canaria Island (Canary Islands, Spain)[☆]

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ABSTRACT

Organic ultraviolet (UV) filters are used in personal care products, but they are also added to industrial products and are constantly released to the environment. This study analyses the occurrence of 8 widely used organic UV filters in seawater from three beaches on the Gran Canaria Island (Spain) and in three wastewater treatment plants (WWTPs) by taking samples from influents and effluents. It also discusses the target compounds' post-treatment removal efficiencies. Sampling was carried out for 6 months and analytes were extracted by solid phase extraction with Sep-pak C18 cartridges. They were determined by ultra-high performance liquid chromatography coupled to mass spectrometry in tandem. The potential environmental hazard associated with the found concentrations was also assessed for marine organisms.

Different target compounds were detected on the analysed beaches and in the wastewater. Benzophenone-3 (BP3) was the most recurrent compound in the seawater samples (frequency detection of 83%) and also in wastewater influents and effluents (measured in all the samples). However, the highest concentrations for seawater ($172 \mu\text{g L}^{-1}$) and influent wastewater ($208 \mu\text{g L}^{-1}$) corresponded to octocrylene, while methylene bis-benzotriazolyltetramethylbutylphenol was the compound most concentrated in secondary treatment effluent ($34.0 \mu\text{g L}^{-1}$) and BP3 in tertiary treatment effluent ($8.07 \mu\text{g L}^{-1}$). All the analysed samples showed that at least one target UV filter was present.

Regarding the removal efficiencies of these compounds in the studied WWTPs, consistent differences between the target compounds were observed in influent concentration terms, where the average removal rates were higher than 50% for most of the compounds. Conventional treatment is unable to completely remove many studied compounds, while tertiary treatment acts as an additional elimination for some of them.

An environmental hazard quotient above 1 was found for octocrylene, benzophenone-3 and 4-methylbenzylidene camphor, which indicates a potential high hazard for living species if these compounds are present.

1. Introduction

Ultraviolet (UV) filters are used to protect skin from harmful UV radiation effects, and they are added to different personal care products (PCPs) and industrial goods. However, some UV filters cause undesired dermatological effects, such as dermatitis or allergies (Giokas et al., 2007). The maximum concentration of each UV filter is controlled in the European Union by Regulation no. 1223/2009 (EC, 2009), and ranges between 4% and 15% for organic UV filters and is approximately 25% for inorganic UV filters. Combinations of filters are used to gain protection for both solar radiation regions: UVA and UVB. Eleven families of

organic UV filters have been established according to their main physico-chemical properties (Ramos et al., 2015). Given their extensive use, hundreds of tonnes of organic UV filters are released to the environment annually (Danovaro et al., 2008), and means that they are considered a new kind of environmental pollutant (Emmanouil et al., 2019). In addition, most exhibit some priority organic pollutant characteristics, such as high octanol-water coefficients ($\text{Log } K_{\text{OW}} > 3$) and stability against biotic degradation (Vila et al., 2017).

Organic UV filters follow two main pathways to reach the aquatic environment: i) by being directly washed off from skin and clothing during recreational activities; ii) by being indirectly released in treated

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wastewater from domestic use (showering, washing, etc.), industrial discharge and runoff (Molins-Delgado et al., 2014). UV filters are detected worldwide in several matrices: fresh (Ramos et al., 2015; Sereshti et al., 2020; Nouri et al., 2020) and marine environments (Cadena-Aizaga et al., 2020), sludges (Ramos et al., 2016) and even tap water (Díaz-Cruz et al., 2012). The study performed by Downs et al. (2016) reports concentrations in seawater of up to $\text{mg}\cdot\text{L}^{-1}$ level, in which the most obvious input is the direct one. Other inputs to the marine environment are presented in Fig. 1. In recent years, organic UV filters have become an increasing concern because they show a tendency to bioaccumulate at different trophic levels (Cadena-Aizaga et al., 2020). These compounds have already been reported in marine biota (Ramos et al., 2015), and even in humans (Fivenson et al., 2020). Some organic UV filters like 4-methylbenzylidene camphor (4MBC) caused impaired reproduction, increased mortality in benthic organisms (Schmitt et al., 2008), and they produce coral bleaching (Danovaro et al., 2008) and induce malformation and mortality in early fish stages (Araújo et al., 2018). Benzophenone-3 (BP3) and 4MBC have a reported similar toxicity to metals to marine organisms (Paredes et al., 2014) so it is important to understand their fate and behaviour in the environment.

Different methodologies for extracting and determining organic UV filters from environmental samples have been used (Ramos et al., 2015; Cadena-Aizaga et al., 2020). Solid phase extraction (SPE) technique is one of the most widely applied techniques as it integrates both pre-concentration and extraction in one step (Gago-Ferrero et al., 2013a). Organic UV filters analyses are performed by gas (GC) or liquid chromatography (LC) coupled to mass spectrometry detectors (MS). Often LC coupled to MS detection in tandem (MS/MS) is the best option because it yields high sensitivity for a wide range of compounds (Ramos et al., 2015; Cadena-Aizaga et al., 2020). Moreover, some organic UV filters cannot be determined by GC for their low volatility and thermal stability (Sánchez-Brunete et al., 2011).

The Gran Canaria Island is part of Canary archipelago (Spain) located in the Atlantic Ocean. This is the perfect scenery to carry out environmental studies about these compounds because tourism (both national and international (de Turismo, 2021)) is one of the mainstays of its economy and its beaches are used almost all year long. Therefore, its coast is subjected to the intense and continuous direct input of organic UV filters. However, only a few works (García-Guerra et al., 2016;

Sánchez Rodríguez et al., 2015; Montesdeoca-Esponda et al., 2012; Montesdeoca-Esponda et al., 2013) have been performed on their occurrence in and impact on the aquatic systems in this geographical area, and have focused mostly on benzotriazole UV stabilisers.

Hence the aim of this work was to study the presence of eight organic UV filters in seawater and wastewater samples taken from the Gran Canaria Island. Three beaches and three WWTPs were monitored for 6 months (May–October 2019) to evaluate spatio-temporal variation and the efficiency of the elimination achieved with the sewage treatments for each target compound was discussed. Finally, the environmental hazard associated with the found concentrations was assessed for different aquatic organisms.

2. Materials and methods

2.1. Reagents and materials

Eight analytical-grade (purity $\geq 99\%$) organic UV filters (Table 1), which ranges of concentration are shown in Table S1, namely homosalate (HMS), 4-MBC, BP3, drometrizole trisiloxane (DTS), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl *p*-methoxycinnamate (IMC), and methylene bis-benzotriazolyltetramethyl butylphenol (MBP) were purchased from Sigma-Aldrich (Madrid, Spain). Methanol (MeOH), acetone, acetonitrile (ACN), water and formic acid (LC-MS grade) were supplied by Panreac Química (Barcelona, Spain). Stock solution (250 mg L^{-1}) was prepared in acetone and stored in amber glass bottles in a freezer until used. Working solutions were prepared in MeOH daily. Membrane filters (0.22 and $0.45 \mu\text{m}$) were purchased from Millipore (Cork, Ireland). For the SPE technique, three cartridges were tested: 200 mg Oasis HLB; 500 mg Sep-pak C18 from Waters (Madrid, Spain); 500 mg Strata-X from Phenomenex (Madrid, Spain).

2.2. Sample collection

Three different beaches were selected for their particular geomorphological characteristics, their level of tourist pressure and type of users: Las Canteras, Arinaga and Playa del Inglés. Sampling lasted 6 months (May–October 2019) at low tide around the noon; these months

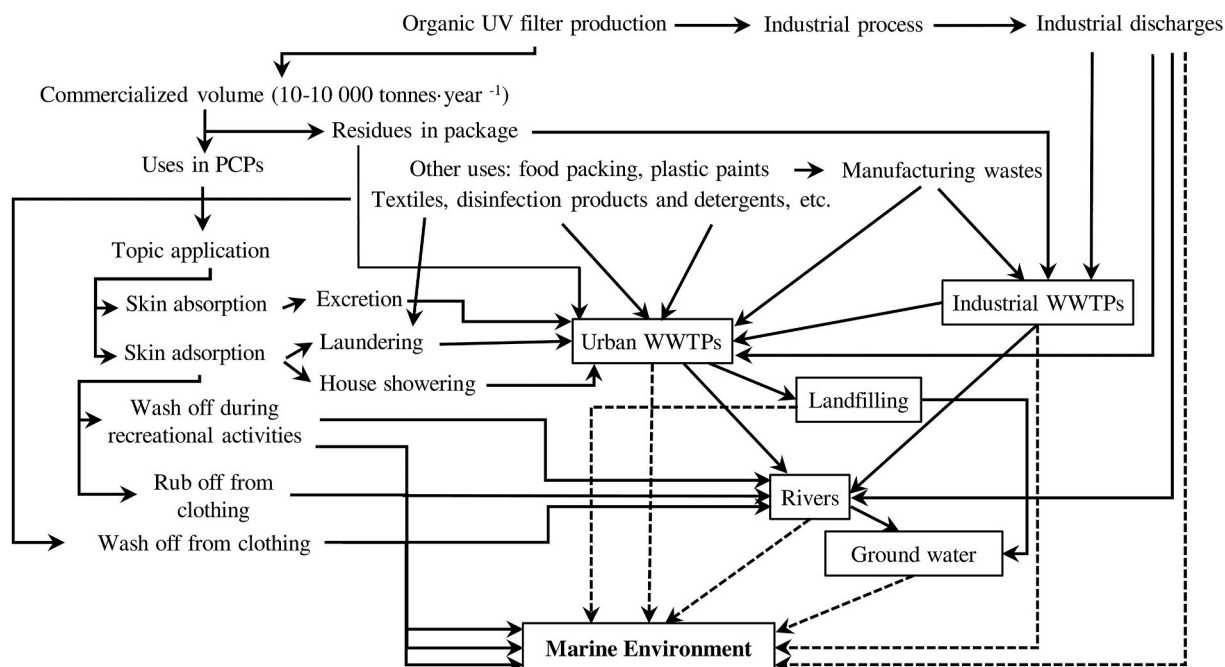
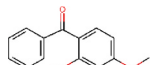
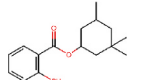
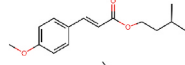
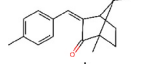
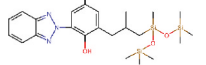
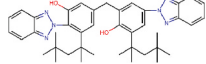
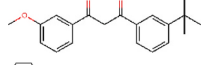
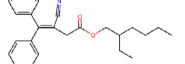


Fig. 1. Organic UV filters inputs to the marine environment. Dotted line refers to indirect inputs.

Table 1
Main characteristics and structure of the eight organic UV filters subjected to study.

Family	INCI name ^a /Other common names	Abbreviations	Structure	CAS number	Molecular formula	Molecular weight	Log K _{ow}	pKa	Solubility (g·L ⁻¹) ^g	EU production ^h
Benzophenones	Benzophenone-3/Oxybenzone	BP3/BZ3/HMB/OBZ		131-57-7	C ₁₄ H ₁₂ O ₃	228,24	3.79 ^b	7.56 ^e	0.21	LPV
Salicylates	Homosalate	HMS/HS		118-56-9	C ₁₆ H ₂₂ O ₃	262,34	6.16 ^c	8.09 ^e	0.02	HPV
Cinnamates	Isoamyl <i>p</i> -methoxycinnamate/Amiloxate	IMC/IAMC		71 617-10-2	C ₁₅ H ₂₀ O ₃	248.32	4.33 ^c	–	0.06	LPV
Camphor derivatives	4-methylbenzylidene camphor/Enzacamene	4MBC/MBC		36 861-47-9/ 38 102-62-4	C ₁₈ H ₂₂ O	254,37	4.95 ^c	–	5.1 × 10 ⁻³	LPV
Benzotriazoles	Drometrizole trisiloxane	DTS		155 633-54-8	C ₂₄ H ₃₉ N ₃ O ₃ Si ₃	501,84	10.82 ^d	9.72 ^f	1.3 × 10 ⁻⁵	–
	Methylene bis-benzotriazolyltetramethylbutylphenol/Bisotrizole	MBP/UV 360/MBBT/MBT		103 597-45-1	C ₄₁ H ₅₀ N ₆ O ₂	658,87	12.46 ^d	7.56 ^f	3 × 10 ⁻⁸	LPV
Dybenzoyl methane derivatives	Butyl methoxydibenzoylmethane/Avobenzene	BMDBM/BDM/BMDM/BMBM/AVO/AVB		70 356-09-1	C ₂₀ H ₂₂ O ₃	310,39	4.51 ^c	9.74 ^e	0.037	HPV
Crylenes	Octocrylene	OC/OCR/OCT		6197-30-4	C ₂₄ H ₂₇ NO ₂	361,48	6.88 ^c	–	2 × 10 ⁻⁴	HPV

^a INCI International Nomenclature for Cosmetic Ingredients.

^b Experimental value from Syracuse Research Corporation database.

^c Estimated values from Syracuse Research Corporation database.

^d Calculated by use of Estimation Program Interface (EPI) suite v4.11 (2012).

^e Software calculated value, from SciFinder Scholar Database 2006.

^f Values obtained from Chemizalze website.

^g From Díaz-cruz et al. (2012) in water at 25 °C.

^h From European Chemicals Agency (ECHA), low production volume (LPV) between 10 and over 100 tonnes·year⁻¹ and high production volume (HPV) between 1000 and 10 000 tonnes·year⁻¹ of chemicals produced or imported in the European economic area.

were selected to find possible seasonal variation during pre-summer (May–June), summer (July–August) and post-summer (September–October) periods. The seawater samples were collected in 2-L amber glass bottles using gloves, at 2 m from the coast in the middle of the bathing zone and approximately at 50 cm below the water surface (Fagervold et al., 2019).

Las Canteras beach is located on the northeast coast of the Gran Canaria Island (sample location 1, SL1, Table S2). It is an urban beach used mainly by locals and moderately by international tourists approximately all year long (de Turismo, 2021), where the most intense tourism takes place in the summer. The main characteristic of this beach is the presence of a natural barrier running in parallel to the coast, which leads to a lower water renovation rate at low tide than at high tide given the almost null wave action (Perez-Torrado and Mangas, 1994). For this reason, local fauna might be affected by pollutants' long residence time.

The Arinaga beach is located on the southeast coast of the Gran Canaria Island (SL2, Table S2). It is principally used by locals and barely used by international tourists (de Turismo, 2021). It is an open beach with intense wind and a strong swell influence due to the north-northeast effect of Trade winds and the Canary Current (Alonso et al., 2001), which make water renewal easy.

The Playa del Inglés beach is located on the south coast of the Gran Canaria Island (SL3, Table S2). It is an open beach characterised by mass international tourism formed essentially by northern Europeans according to the Tourism Agency of Gran Canaria (de Turismo, 2021). These tourists often use sunscreens with a high sun protection factor. On this beach, trade winds and the Canary Current effect are less pronounced (Alonso et al., 2001), and this creates a peaceful zone with light swells. This beach has artificial barriers. SL3 is used almost all year, and more intensely by international tourists than locals in winter, but more intensely by national tourists than international ones in summer. Moreover, this beach could be influenced by treated sewage discharges (de Canarias, 2021).

The wastewater samples were taken from the influents and effluents in three different WWTPs on the Gran Canaria Island, namely WWTP1, WWTP2 and WWTP3 (Table 2), located in the Las Palmas city, in the Arinaga village and in the San Bartolomé de Tirajana municipality, respectively. Facilities comprise primary and secondary treatments, with the latter based on conventional activated sludge. The tertiary treatment, performed by microfiltration, is only available in WWTP2. Samples were collected by the WWTP staff at the same hour every month in 2-L amber glass bottles. More detailed information on the WWTPs treatments and characteristics is available in Table 2.

2.3. Pre-treatment and extraction procedures

Seawater and wastewater samples were acidified with formic acid to pH = 3 and pH = 2 respectively to inhibit microbial activity and were stored at fridge in amber glass bottles until their analysis in the maximum period of one month. Seawater samples were filtered through 0.22 µm membrane filters and wastewater samples by 0.45 µm cellulose filters.

Sample extraction was done by the SPE procedure. C18 cartridges were conditioned before each extraction with 5 mL of MeOH followed by 5 mL of Milli-Q water. For seawater, 700 mL of seawater at pH 3 were

passed through a cartridge, while 250 mL were used for wastewater at pH 7. A cleaning step (salt or impurity elimination) was carried out with 5 mL of Milli-Q water. Then cartridges were dried in a vacuum for 1 min and the retained analytes were eluted with 5 mL of MeOH:ACN (1:1, v/v) for seawater and 5 mL of MeOH for wastewater.

2.4. Instrumental analysis

The selected organic UV filters were determined in an ACQUITY UHPLC system equipped with a binary solvent manager, a thermostated autosampler, a BEH C18 column (50 × 2.1 mm, 1.7 µm particle size) and a tandem triple quadrupole mass spectrometer detector (MS/MS) with electrospray ionisation (ESI). All the components were controlled by the MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain). The ESI parameters were fixed as follows: capillary voltage at 4 kV, 15 V cone voltage, 120 °C source temperature, 450 °C desolvation temperature and 500 L h⁻¹ desolvation gas at. Nitrogen and argon gases were used for desolvation and collision, respectively. Detailed MS/MS conditions are found in the Supplementary Material (Table S3).

The mobile phase consists in MeOH (A) and water (B) of LC-MS grade with 0.1% (v/v) formic acid, each at a flow rate of 0.3 mL min⁻¹. To separate analytes, the following gradient was employed; starting with 25% A: 75% B, which was left for 3 min and then lowered to 0% of A in 2 min and held for 1 min. Finally, A was increased to 25% for 1 min and held for 1 min for the next injection. The injected extract volume was 10 µL.

2.5. Environmental hazard

Toxicological data for the target compounds in marine species are necessary for an environmental hazard quantification. Nevertheless, toxic effects studies are not available for several organic UV filters. All the existing harmful data on target compounds for marine organisms belonging to different trophic levels are shown in Table 3. A marine gram-negative bioluminescent bacterium (*Photobacterium phosphoreum*), which usually lives in symbiosis with marine organisms, has been studied for the toxic effect of BP3 (Liu et al., 2015). Two microalgae (*Isochrysis galbana* and *Skeletonema pseudocostatum*) of the marine plankton have been used to test the toxicity effects of 4MBC, BP3 and OC (Paredes et al., 2014; Giraldo et al., 2017; Petersen et al., 2014). A copepod (crustacean) was exposed to 4MBC for four generations, which reports toxicity in development and reproductive (Chen et al., 2018). Two bivalve molluscs, a mussel (*Mytilus galloprovincialis*) and a clam (*Ruditapes philippinarum*), have also been investigated to analyse the effects of OC, 4MBC and BP3, and 4MBC, respectively (Giraldo et al., 2017; Santonocito et al., 2020). One echinoderm, the sea urchin *Paracentrotus lividus*, have been exposed to BP3, 4MBC and OC to know its toxic effects on larval stages (Giraldo et al., 2017; Petersen et al., 2014). The carnivore arthropod crustacean *Siriella armata* has also been exposed to 4MBC and BP3 (Paredes et al., 2014). Finally, fertilised eggs of a flatfish (*Solea senegalensis*) have been exposed to 4MBC to analyse mortality, malformations, length, behaviour and biochemical markers in the larval stage (Araújo et al., 2018).

However, as compounds like BMDBM, DTS, HMS and MBP have a

Table 2
Main characteristics of studied WWTPs.

WWTPs	Treatments ^a		Inhabitants equivalents ^b	Secondary effluent characteristics ^a		
	Secondary	Tertiary		Discharge level (m)	Emissary length (m)	Emissary flow (m ³ ·h ⁻¹)
WWTP1	Activated sludge	–	200 749	- 41	2090	540
WWTP2	Activated sludge	Microfiltration	134 000	- 27	930	355
WWTP3	Activated sludge	–	103 315	- 19	350	147

^a Data obtained from Gobierno de Canarias (<https://www.pilotajelitoralcanario.es>).

^b Data obtained from iagua (<https://www.iagua.es>).

Table 3

Normalized target organic UV filters concentrations measured in the three studied WWTPs ($\mu\text{g}\cdot\text{d}^{-1}\cdot 1000\text{ inhabitant}^{-1}$).

Date	UV filters	WWTP 1		WWTP 2			WWTP 3	
		Influent	Secondary	Influent	Secondary	Tertiary	Influent	Secondary
May-19	4MBC	311 ± 16.9	76.5 ± 5.40	236 ± 4.88	96.8 ± 1.77	49.2 ± 5.36	596 ± 77.8	44.4 ± 4.16
	BP3	2582 ± 241	474 ± 14.6	5266 ± 354	791 ± 90.4	565 ± 4.41	8572 ± 535	263 ± 5.77
	HMS	nd	nd	437 ± 31.5	37.2 ± 0.72	20.2 ± 2.41	2629 ± 124	nd
	DTS	315 ± 44.7	10.1 ± 1.33	110 ± 15.1	48.1 ± 1.68	37.2 ± 2.82	205 ± 24.7	nd
	OC	217 ± 27.6	nd	2396 ± 138	95.7 ± 7.72	nd	12 327 ± 461	84.7 ± 10.5
	BMDBM	4804 ± 413	140 ± 10.3	2349 ± 172	410 ± 1.10	nd	7423 ± 296	125 ± 3.25
	IMC	53.7 ± 8.37	38.2 ± 3.78	97.5 ± 2.48	74.3 ± 11.3	38.0 ± 2.56	92.0 ± 6.27	11.4 ± 0.94
	MBP	nd	nd	nd	nd	nd	1293 ± 80.0	nd
June-19	4MBC	nd	nd	99.5 ± 14.4	29.7 ± 4.48	18.2 ± 1.10	623 ± 65.6	42.8 ± 5.57
	BP3	4490 ± 654	338 ± 27.0	3435 ± 467	791 ± 50.4	821 ± 58.0	6575 ± 250	259 ± 24.0
	HMS	241 ± 28.2	nd	28.3 ± 3.62	nd	138 ± 3.27	1822 ± 215	nd
	DTS	213 ± 27.1	25.2 ± 2.65	22.4 ± 2.21	15.1 ± 1.72	nd	124 ± 18.2	nd
	OC	1184 ± 109	118 ± 16.0	634 ± 38.2	148 ± 22.4	144 ± 16.4	9335 ± 706	72.4 ± 8.77
	BMDBM	3687 ± 296	216 ± 31.8	3454 ± 356	251 ± 15.5	162 ± 11.7	6371 ± 697	165 ± 24.3
	IMC	55.3 ± 8.30	26.6 ± 2.17	74.0 ± 8.11	56.5 ± 8.87	34.3 ± 3.59	96.3 ± 1.55	10.8 ± 0.59
	MBP	nd	nd	1327 ± 154	826 ± 117	nd	nd	nd
July-19	4MBC	85.0 ± 11.7	34.3 ± 4.80	239 ± 25.1	16.2 ± 0.92	155 ± 16.3	474 ± 35.8	nd
	BP3	3004 ± 209	324 ± 29.8	2786 ± 98.8	903 ± 77.1	890 ± 28.9	7838 ± 93.1	200 ± 5.24
	HMS	172 ± 24.5	nd	148 ± 18.8	98.5 ± 10.6	16.9 ± 0.18	2590 ± 74.1	nd
	DTS	104 ± 12.2	nd	177 ± 14.3	nd	139 ± 8.30	234 ± 31.6	24.0 ± 0.59
	OC	927 ± 62.0	144 ± 18.5	2984 ± 128	189 ± 11.0	35.2 ± 2.23	8877 ± 308	21.0 ± 2.30
	BMDBM	3965 ± 276	292 ± 30.1	390971.0	288 ± 33.1	233 ± 2.42	6632 ± 493	100 ± 10.5
	IMC	74.6 ± 6.39	18.5 ± 1.73	28.2 ± 1.81	31.3 ± 1.53	25.5 ± 2.87	113 ± 4.80	5.03 ± 0.80
	MBP	1847 ± 222	1091 ± 144	nd	nd	nd	1207 ± 98.2	nd
August-19	4MBC	nd	nd	317 ± 13.1	nd	nd	386 ± 44.0	43.9 ± 6.28
	BP3	3444 ± 325	294 ± 26.2	2682 ± 318	825 ± 14.2	740 ± 29.0	5882 ± 266	385 ± 26.3
	HMS	318 ± 45.7	nd	54.2 ± 6.87	216 ± 33.0	nd	1688 ± 77.6	26.1 ± 3.12
	DTS	nd	nd	147.8 ± 16.0	nd	93.4 ± 11.1	205 ± 29.2	nd
	OC	913 ± 126	88.6 ± 3.65	436 ± 32.4	217 ± 11.6	200 ± 15.0	7518 ± 675	22.9 ± 2.04
	BMDBM	4199 ± 590	132 ± 19.5	3982 ± 576	190 ± 12.1	107 ± 5.0	5319 ± 79.4	136 ± 18.2
	IMC	100 ± 8.09	19.5 ± 1.26	56.8 ± 1.22	42.6 ± 5.20	29.0 ± 0.97	123 ± 8.07	nd
	MBP	nd	nd	nd	nd	nd	1596 ± 28.6	1325 ± 51.1
September-19	4MBC	nd	nd	nd	nd	nd	454 ± 29.5	nd
	BP3	2330 ± 79.3	488 ± 27.2	2828 ± 300	479 ± 16.4	432 ± 35.5	6951 ± 307	244 ± 4.64
	HMS	nd	nd	140 ± 10.4	nd	72.5 ± 10.2	1345 ± 85.0	nd
	DTS	nd	nd	223 ± 26.7	nd	nd	36.8 ± 6.31	nd
	OC	780 ± 17.8	99.9 ± 6.60	3219 ± 489	224 ± 1.10	nd	5549 ± 119	nd
	BMDBM	3423 ± 456	173 ± 7.78	3914 ± 100	220 ± 22.1	nd	5161 ± 524	168 ± 1.87
	IMC	55.4 ± 6.71	41.5 ± 6.48	53.4 ± 8.48	41.3 ± 4.82	nd	87.4 ± 13.5	3.40 ± 0.45
	MBP	nd	nd	nd	nd	nd	2637 ± 182	2013 ± 13.3
October-19	4MBC	98.9 ± 14.9	nd	118 ± 3.89	16.4 ± 3.21	61.3 ± 0.78	349 ± 17.3	nd
	BP3	2189 ± 95.8	308 ± 17.4	2717 ± 331	504 ± 34.5	483 ± 1.68	5215 ± 316	187 ± 20.9
	HMS	133 ± 21.3	nd	87.7 ± 11.2	nd	47.1 ± 3.05	540 ± 60.0	nd
	DTS	117 ± 17.5	nd	210 ± 30.0	31.2 ± 3.58	91.7 ± 4.36	nd	nd
	OC	1120 ± 104	72.1 ± 8.72	1842 ± 139	129 ± 4.47	69.9 ± 6.12	1277 ± 151	42.9 ± 5.31
	BMDBM	4003 ± 419	83.2 ± 6.93	3632 ± 517	242 ± 19.9	nd	3021 ± 435	86.7 ± 12.1
	IMC	22.2 ± 2.89	10.4 ± 0.65	66.0 ± 2.33	21.3 ± 0.60	19.1 ± 1.46	67.6 ± 1.25	nd
	MBP	nd	nd	1641 ± 155	967 ± 17.1	215 ± 22.7	2041 ± 164	nd
Detection frequencies (%)	4MBC	50	33	83	67	67	100	50
	BP3	100	100	100	100	100	100	100
	HMS	67	0	100	50	83	100	17
	DTS	67	33	100	50	67	83	17
	OC	100	83	100	100	67	100	83
	BMDBM	100	100	100	100	50	100	100
	IMC	100	100	100	100	83	100	67
	MBP	17	17	33	33	17	83	33
Percentage of positive samples (%)	75	58	90	75	67	96	58	

nd: not detected.

high Log K_{ow} (>4.51), they could affect aquatic organisms at lower concentrations (Sánchez Rodríguez et al., 2015). In addition, the joint effects of several additives, metabolites, and their degradation products, should be considered towards a more realistic approach to deal with the environmental hazard because a mixture of these organic UV filters is found in seawater and marine organisms (Cadena-Aizaga et al., 2020; Molins-Delgado et al., 2018).

Environmental hazard associated with the concentrations measured

in seawater were quantified for those compounds for which toxic data are available (BP3, 4MBC and OC). The hazard quotient (HQ) was quantified by the following expression (Paredes et al., 2014):

$$HQ = MEC/PNEC$$

where MEC is the measured environmental concentration in seawater and PNEC is the predicted non-effect concentration. PNEC is established on the non-observed effect concentration (NOEC), the median lethal

concentration (LC₅₀) or the median effective concentration (EC₅₀), which are divided by an appropriate assessment factor (AF) according to the Technical Guidance Document of the European Commission of Risk Assessment (Commission, 2003). In this case, and based on the available information for the target compounds, the chosen AF was 50 (Commission, 2003; Carve et al., 2021). HQs were calculated for each marine species and location using a mean value for each period (pre-summer, summer and post-summer).

3. Results and discussion

3.1. Extraction process

The extraction and elution parameters that potentially affected the SPE process were optimised for both matrices (seawater and wastewater) to achieve the best extraction efficiencies for the target UV filters. Firstly, the different sorbents employed in SPE were tested. Once the cartridge was selected, the extraction and desorption parameters were optimised by an experimental design in the statistical Minitab 17 software, in which the influence of each variable and their possible correlations were studied.

3.2. Extracting organic UV filters from seawater

Due to the target compounds' different physico-chemical characteristics, three frequently used cartridges to extract organic UV filters from seawater were tested: OASIS HLB (Paredes et al., 2014), Strata-X (Sánchez Rodríguez et al., 2015) and Sep-pak C18 (Goksøyr et al., 2009). The initial conditions employed to test cartridges were: sample volume, 250 mL; extractant volume and type; 5 mL of MeOH; two pH values of 3 and 7. After comparing the results obtained with each combination, the best recoveries were obtained for pH 3. Then different elution organic solvents were examined, i.e., MeOH, ACN and an MeOH:ACN mixture (1:1, v/v). The best recoveries for most compounds were achieved with a C18 cartridge and the MeOH:ACN (1:1, v/v) mixture as the eluent (Figure S1). Therefore, the conditions chosen from this step were a C18 cartridge, pH 3 and MeOH:ACN (1:1, v/v) as the elution solvent.

In a second stage, other extraction parameters were optimised by a 2³ experimental design (three variables, two levels). The following conditions were tested: 100 mL and 400 mL of the sample volume, 1 mL and 5 mL of MeOH:ACN (1:1, v/v) as eluents, and 0% and 3% of salt addition. A Pareto chart of the standardised effects was built (an example of BMDBM in Figure S2, where the most influential variable is marked in blue). The correlations between the different variables were analysed, where 0 means no effect and 1 is the maximum positive effect. Solvent volume and sample volume led to the highest correlation with between 0.66 and 0.88 and between 0.18 and 0.53, respectively. Regarding the eluent volume influence, 1 mL did not suffice to recover analytes, while better recoveries were obtained for 5 mL. The same behaviour was observed for sample volume as bigger volumes provided higher recoveries. Low or negative effects were obtained for ionic strength.

Ionic strength was ruled out for the second experimental design. Then the two most influential variables were studied in-depth using a 3² factorial design (two variables, three levels) for sample volume (250, 500, 700 mL) and eluent volume (4, 5, 6 mL). The best recoveries were gained by using 700 mL of the sample volume and 5 mL of eluent. The response surfaces for the effect of the variables on the extraction of BMDBM are seen in Figure S3, which was comparable for all the target compounds. Based on all these results, the following seawater extraction conditions were chosen: 700 mL of sample volume, 5 mL of MeOH:ACN (1:1, v/v) as the eluent, pH 3 and 0% ionic strength. Under these conditions, a preconcentration factor of 140 times was achieved.

3.3. Extracting organic UV filters from wastewater

As wastewater is a different and more complex matrix than seawater, the extraction conditions were also optimised for this kind of matrix. The same cartridges (HLB, Strata-X and Sep-pak C18) were tested. The fixed conditions of pH, sample volume, and eluent for this first attempt were 3, 250 mL and 5 mL of MeOH, respectively. As expected, the best recoveries were obtained with the C18 cartridge (Figure S4).

After selecting the cartridge, a 2³ experimental design was followed. The three studied variables were pH, sample volume and ionic strength, and the two levels were 3 and 7, 100 mL and 250 mL and 0% and 5%, respectively. A Pareto chart analysis was performed for all the target compounds (an example of BMDBM in Figure S5). From the obtained results, the most significant variable for analytes' responses was ionic strength. The effect was clearly negative (between -0.8 and -0.9), except for MBP, which was slightly positive (0.3). Sample volume (<0.27) and pH (<0.19) did not show any significant effect for most compounds. Given the negative effects of ionic strength, this variable was set at 0%. The selected pH was 7 because this condition reported slightly better recoveries for BP3, IMC and HMS. Sample volume was established at 250 mL to obtain the highest possible preconcentration. No bigger volumes were studied because large volumes can clog cartridges. Thus the fixed conditions were: a C18 cartridge, 0% ionic strength, 250 mL of sample volume and pH 7.

After setting the extraction conditions, the elution conditions were optimised and, therefore, a 3² factorial design was run. The variables under study were eluent volume and eluent solvent: 2, 4 and 6 mL of MeOH, and ACN and MeOH:ACN (1:1, v/v) mixtures, were studied. Regarding the eluent volume, 2 mL gave the lower recoveries for all the tested eluents, and 5 mL led to satisfactory results. As for eluent type, ACN obtained the lowest recoveries for all the tested volumes (Figure S6). Using MeOH and MeOH:ACN (1:1, v/v), five compounds (4MBC, BP3, BMDBM, IMC, MBP) resulted in better or comparable recoveries using only MeOH. Thus, MeOH was chosen to achieve the simplest and fastest method. According to the results of the experimental designs, the optimum conditions for extracting target UV filters from wastewater were: 250 mL of sample, pH 7, 0% ionic strength and 5 mL of MeOH as the extractant, which gave a concentration factor of 50.

3.4. Quality assurance

The linearity, recovery, precision, limits of detection and limits of quantification were evaluated under the optimum extraction conditions for each water type for a mixture of standard solutions. Each value corresponded to the mean of three replicates.

Clean seawater was used to build calibration curves by the matrix match calibration method at eight concentration levels of a mixture of the target UV filters within the 0.025–250 µg L⁻¹ Range. The linear correlation coefficient obtained for each compound within this range was >0.99 (Table S4). For wastewater, as the target compounds were present in the influent, secondary and tertiary effluents, a standard additions method was followed to build the calibration curves in each water type. Eight concentration levels of a mixture of the target compounds within the 0.05–250 µg L⁻¹ range were employed. Satisfactory linear range coefficients (>0.99) were reached for each compound in the three wastewater types (Table S4).

Extraction efficiencies were studied for seawater and for the three wastewater types (influent, and secondary and tertiary effluents) at two concentration levels (Table S5). In the case of seawater the concentrations used were 0.05 µg L⁻¹ and 200 µg L⁻¹, while for the influent samples 0.3 µg L⁻¹ and 200 µg L⁻¹, and for secondary and tertiary treatment effluent were 0.1 µg L⁻¹ and 10 µg L⁻¹. Recoveries ranged from 43.8% to 100% for seawater. In the influent and secondary effluent samples from WWTPs, values were above 50.6% and 65.1%, respectively (except for MBP, which was around 20%). In the samples from the tertiary effluent, recoveries were between 26.0% and 98.5%.

The intraday ($n = 9$) and interday ($k = 3$) repeatability of the developed method were expressed as relative standard deviation and were performed for each water type at the two concentration levels mentioned above (Table S6). Intraday and interday precision ranged from 0.02 to 13.9% for seawater, from 0.50 to 13.9 for influent, from 2.30 to 12.5 for the secondary effluent and from 4.49 to 12.4 for the tertiary effluent.

Method limits of detection (MLODs) and quantification (MLOQ) were calculated for each compound from the signal to noise (S/N) by assuming a minimum detectable limit of 3 and 10 times the S/N ratio, respectively. MLODs ranged from 11.3 ng L^{-1} to 36.4 ng L^{-1} and the MLOQs between 35.9 and 121.3 ng L^{-1} for the eight target compounds in seawater, while the MLODs ranged from 24.6 ng L^{-1} to 555.6 ng L^{-1} and the MLOQs between 52.1 ng L^{-1} and 1851.9 ng L^{-1} for wastewater samples (Table S7).

3.5. Occurrence of organic UV filters in seawater and wastewater

The developed method was applied to determine the target analytes in the seawater and wastewater from the Gran Canaria Island. Samples were collected from three different beaches and in the influents and effluents of three WWTPs, for 6 months (May–October 2019). The found concentrations and detection frequencies for all the organic UV filters analysed in seawater and wastewater are detailed in Table S8 and Table S9, respectively.

3.5.1. Seawater

Seven of the eight compounds were detected with different frequencies on several beaches (Table S8), while MBP was detected only in one location and in one sample. Detection frequencies ranged from 6% for MBP to 83% for BP3, with concentrations levels between $0.07 \text{ } \mu\text{g L}^{-1}$ and $172 \text{ } \mu\text{g L}^{-1}$. BP3 and IMC were the most frequently detected (83%

and 78%, respectively) with concentration ranges from $0.16 \text{ } \mu\text{g L}^{-1}$ to $20.5 \text{ } \mu\text{g L}^{-1}$ and from $0.07 \text{ } \mu\text{g L}^{-1}$ to $4.27 \text{ } \mu\text{g L}^{-1}$, respectively. At least one compound was detected in each sample (Table S8).

The high detection frequency of BP3 and IMC could be explained by these compounds presenting the lowest Log K_{ow} (3.79 and 4.33, respectively) and the highest water solubility of all the studied compounds (Table 1). BP3 is one of the most widely used UV filters, and is allowed in all countries (Tarazona et al., 2010). It also has a slower photodegradation rate than other organic UV filters (Santos et al., 2012). In the study by Tsui et al. (2014a), BP3 was the most widely detected compound in the different sampled places, including the Arctic. In a recent review, a recurrent compound was also reported in seawater, with a concentration up to the mg L^{-1} level in the samples taken in summer, which demonstrates its worldwide distribution and occurrence (Cadena-Aizaga et al., 2020). Furthermore, the highest concentration corresponded to OC ($172 \text{ } \mu\text{g L}^{-1}$), a compound that is also commonly used in PCPs formulations. A similar concentration ($171 \text{ } \mu\text{g L}^{-1}$) has been detected in seawater on the eastern Spanish coast sampled in summer (Vila et al., 2016a). In contrast, the IMC in that study had the lowest concentrations, between $0.07 \text{ } \mu\text{g L}^{-1}$ and $4.27 \text{ } \mu\text{g L}^{-1}$. IMC is also often used in PCPs formulations (Vila et al., 2016b), but scarce information about its occurrence is available.

According to concentration per location and seasonality, SL1 shows marked temporal variation (Fig. 2), which can be attributed to locals' seasonal habits (Sánchez Rodríguez et al., 2015). The high concentrations of target UV filters in summer at this site can be explained by this beach being more widely used in summer than in winter, and because water remains longer as a result of the natural barrier.

At SL2, the beach also displayed marked seasonal variation, and the August sample had higher concentrations than the post-summer samples. MBP was detected only in October and presented the highest concentration at this site ($146 \text{ } \mu\text{g L}^{-1}$).

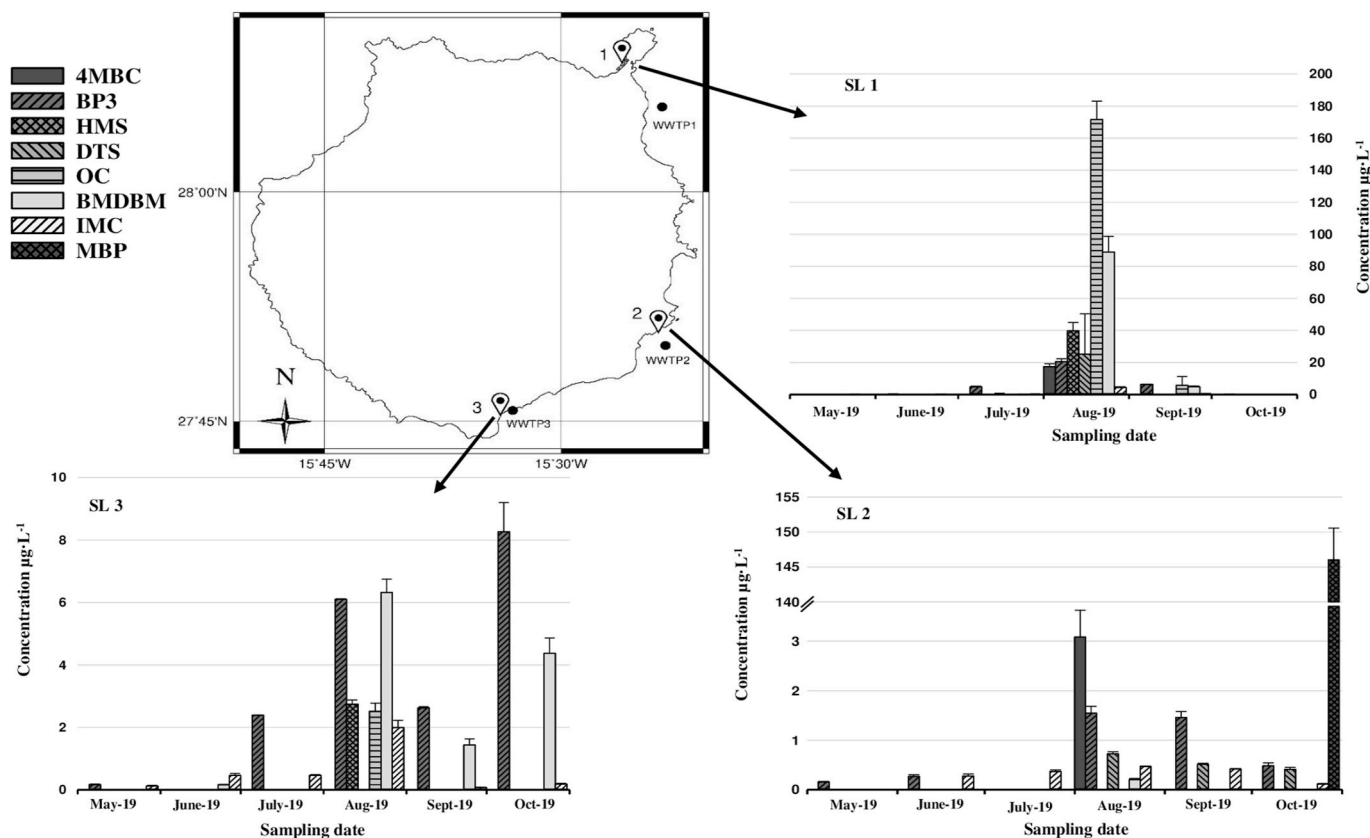


Fig. 2. Measured concentrations of target organic UV filters in seawater samples. Las Canteras beach (SL1), Arinaga beach (SL2), Playa del Inglés beach (SL3). Black points indicate the marine outfall of the three WWTPs.

SL3 receives international tourists all year round. On this beach, a different seasonal variation pattern was observed (Table S8). The second increase during the post-summer period can be explained by this beach being well used by international tourists (mainly north Europeans) during this period. The concentrations measured on this beach are comparable to a “semiclosed” beach in Gran Canaria south, which also has an artificial barrier (Mogán beach) where no seasonal variation is described (Sánchez Rodríguez et al., 2015).

In short, the found organic UV filters and their concentrations seemed to be associated with user type and the water removal rate. Only two studies have been performed on the Canteras beach (SL1) as regards organic UV filters (Sánchez Rodríguez et al., 2015; Montesdeoca-Esponda et al., 2021). By comparing the herein found concentrations to those reported by a study in 2011 (Sánchez Rodríguez et al., 2015), this work detected higher concentrations for OC, BP3, 4MBC, HMS and BMDBM. These variations can be explained by a larger number of tourists in 2019 than in 2011 (25%) (de Turismo, 2021). SL1 appears to be the most contaminated by organic UV filters among the three sampling beaches. This can be attributed to geomorphological characteristics, such as the presence of the natural barrier parallel to its coast that acts as a calm zone where pollutants can be retained. The same behaviour has been described in the same zone in another kind of study, with narrow variation in the micro-meso debris as a result of a less marked marine dynamics influence (McKnight and Rodríguez, 2017). In addition, the concentrations found for BMDBM and BP3 at SL1 were comparable to those reported in other studies carried out in other coastal areas of Spain in summer (Vila et al., 2016b) and in other areas like Hawaii (Downs et al., 2016).

This is the first time that 4MBC, BP3, DTS, BMDBM, IMC and MBP have been studied on the Arinaga (SL2) and Playa del Inglés (SL3) beaches. For SL2, the concentrations found for all the compounds were lower than for the other beaches (Fig. 2). This can be explained because Arinaga is an open beach that is the most affected by trade winds, which facilitate water exchange, and this could demonstrate that the concentration of organic UV filters depends not only on sunscreen users, but also on the water removal rate (Chisvert et al., 2017). According to this study, SL3 is the second most contaminated point by the target organic UV filters, and the observed variability seems related to the different kind of users.

The relatively high concentrations in seawater reported in this study are attributed to its sampling period (higher concentration in summer) and because beaches were sampled at low tide around noon when high sunscreens are expected to be applied (Tovar-Sánchez et al., 2013).

3.5.2. Wastewater

As mentioned above, the mass production and usage of organic UV filters results in them being extensively released to the aquatic environment from WWTPs, which are often not efficient in removing these emerging pollutants.

In order to compare the found concentrations of the target organic UV filters in the different WWTPs, they were normalized to $\mu\text{g}\cdot\text{d}^{-1}\cdot 1000$ inhabitants⁻¹ by considering the treated wastewater volume and the population served by each WWTP (Table 2). The normalized loads for influent, the secondary and tertiary effluents, as well as the detection frequencies of each compound, are presented in Table 3.

The WWTP2 influent had the highest percentage of detected compounds (90%), followed by WWTP1 (75%) and WWTP3 (67%). BP3, OC, BMDBM and IMC were detected in all the influent samples. OC had the highest input load ($12\,327\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹), followed by BP3 ($8572\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹) and BMDBM ($7423\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹). Even though IMC was measured in all the influent samples, it had the lowest mass load ($22.2\text{--}123\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹). MBP showed the most variable frequency in the influent samples, with a range from 17% to 83% depending on the sampling date, and an input load range of $1207\text{--}2637\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹.

Among the results obtained for the secondary treatment effluent, BP3

and BMDBM were present in all the WWTPs during the sampling period, with loads ranges from 200 to $903\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹ and between 83.2 and $410\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹, respectively. The highest load went to MBP ($2013\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹) although this compound presents a wide variation in its detection frequency (17–33%). The percentage of target compounds detected in the secondary effluents of both WWTP1 and WWTP3 was 58%, and was 75% for WWTP2.

By comparing the results obtained in these two wastewater types (influent and effluent from the secondary treatment), BP3 was present in them all throughout the sampling period. This could be explained by BP3 being one of the most hydrophilic compounds (Ramos et al., 2016). BMDBM was also detected in all the influents and secondary effluents. Regarding the most contaminated influent, WWTP3 showed the highest mass loads for all the compounds, with values falling within the range of $36.8\text{--}12327\ \mu\text{g}\ \text{d}^{-1}\cdot 1000$ inhabitants⁻¹.

While observing the WWTP effluents discharge into the marine environment (indirect input), WWTP1 has a long deep outfall (de Canarias, 2021). Thus, the released water was vastly dilution before reaching the beach. Moreover, its waters from the secondary treatment had the lowest concentration of the studied WWTPs for almost all the compounds, except IMC and MBP.

Previous studies have demonstrated the presence of MBP in marine fish (Montesdeoca-Esponda et al., 2021) and sediment (Montesdeoca-Esponda et al., 2019) taken close to the WWTP2 outfall. This agrees with the results found for this compound in the secondary treatment effluent ($4.17\text{--}9.78\ \mu\text{g}\ \text{L}^{-1}$). Because of its high lipophilicity ($\text{Log}\ K_{ow}$ 7.56), this compound tends to be accumulate in solid samples like sediment (Montesdeoca-Esponda et al., 2019) or is bioaccumulated by fish (Peng et al., 2015). This WWTP presents the highest concentrations in the effluent after the secondary treatment for seven compounds (except MBP) and presented the highest positive samples (75%) of all the secondary effluents. However, this marine outfall should not affect the beach because it is located 1.4 km south, and also due to the direction of the current.

The WWTP3 outfall is a shallow emissary (de Canarias, 2021) located north of SL3 and, thus, currents may carry pollutants to the coast. Therefore, the organic UV filters found in its effluent can affect this area and the WWTP3 secondary effluent may be considered a source of such contamination.

BP3 has been the most reported compound in the influent samples from various WWTPs in different cities of Portugal (Cunha et al., 2015), Hong Kong (Tsui et al., 2014b), Italy (Magi et al., 2013) and Spain (Gago-Ferrero et al., 2013b). BMDBM has also been presented in all the influent samples taken in Hong Kong (Tsui et al., 2014b). This could be explained by the relatively low $\text{Log}\ K_{ow}$, which implies a marked tendency to remain in water (Ramos et al., 2016). Concentrations between $\text{ng}\cdot\text{L}^{-1}$ (Ramos et al., 2016) and $\text{mg}\cdot\text{L}^{-1}$ (Kasprzyk-Hordern et al., 2009) have been found in European countries for influents and effluents, respectively.

In addition, the samples from the WWTP2 tertiary treatment were analysed (Table S9). These samples presented BP3 with a 100% frequency during the sampling period, followed by HMS and IMC with 83%, where the highest concentrations corresponded to BP3 and BMDBM (Table 3). Although the tertiary treatment waters are not released to the marine environment, the presence of organic UV filters should be taken into account because they are used for agricultural purposes. A recent study demonstrates that irrigation water containing four organic UV filters (BP3, BMDBM, OC, octinoxate) inhibit cucumber plant growth and decrease both photosynthesis and plant respiration (Zhong et al., 2020). Three compounds reported by that study in tertiary treatment samples (4MBC, OC and DTS) have also been found in market tomatoes at concentrations up to $45\ \text{ng}\ \text{g}^{-1}$ dry weight. The authors suggest possible contamination coming from irrigation water, although the agricultural conditions for these tomatoes were unknown (Ramos et al., 2020).

3.6. Removal of organic UV filters in WWTP

Removal in conventional WWTPs is variable and depends on substance properties and the applied treatment process. The three studied WWTPs have the same secondary treatment by activated sludge. As mentioned above, the concentrations of organic UV filters found in this study are generally lower by 1–2 orders of magnitude in effluents than in influents. Removal rates were calculated by comparing the concentrations in the influent and the effluent from the secondary treatment. In WWTP2, the removal efficiencies after the tertiary treatment were also calculated (Table S10).

All the target compounds showed different elimination rates after the secondary treatment (Table S10), which agrees with previous works (Ramos et al., 2016; Cunha et al., 2015). Two compounds (OC and 4MBC) had a removal rate between 50% and 100%, and these results agree with those reported in different studies for OC (Balmer et al., 2005; Kupper et al., 2006) and 4MBC (Kupper et al., 2006) by applying the same technology of activated sludge.

Two other compounds (BP3 and BMDDBM) obtained a removal rate of 68–99%, which agrees with other studies (68–93%) for BP3 (Balmer et al., 2005). However, some works report lower removal efficiencies for BMDDBM. Li et al. (2018) report elimination to be lower than 80% and Tsui et al. (2014b) name one of 34% after activated sludge. As BP3 was present in all the analysed wastewater matrices, this compound was selected to highlight removal efficiencies at the different WWTPs (Fig. 3A and B).

Regarding HMS and DTS, a variation in the removal rates between 33% and 100% was observed and these results are comparable to those found in other studies for the same compounds, HMS (>70%) (Tsui et al., 2014b) and DTS (52–76%) (Ramos et al., 2019). The widest variations found in this study were for IMC and MBP (17–100%). A removal rate of 44% was noted in Hong Kong (Tsui et al., 2014b) for IMC and Montesdeoca-Esponda et al. study (Montesdeoca-Esponda et al., 2019) report that part of MBP elimination could be due to its adsorption in particles during treatment because of its high Log K_{ow} .

Although activated sludge is a widely used conventional secondary treatment for wastewater, it shows incomplete removal for organic UV filters and their metabolites, which can prove more toxic than parents (Ramos et al., 2016). Organic UV filters are not easily degraded in

WWTPs due to their physicochemical properties, and they are present in both influent and effluent of WWTPs. This means a low removal efficiency of the wastewater treatments. However, because of the lipophilic character of these compounds ($\log K_{ow} > 5$), many of them may be probably sorbed onto sludge (Ramos et al., 2016). Therefore, as some compounds exhibit poor removal rates after secondary treatment process, a tertiary treatment can be employed. To improve the removal efficiency of WWTPs, the implementation of advanced treatments, such as membrane microfiltration, is a possible solution to obtain high-quality water. As the WWTP2 tertiary treatment is performed by microfiltration, these samples were also analysed. Table S10 shows the average removal rates that vary from 10% to 100% for the different compounds. In addition, another tertiary treatment consisting in filtering fine suspended solids, followed by UV disinfection, performing better removal efficiencies for those compounds with a relatively high Log K_{ow} (Tsui et al., 2014b).

In summary, of the removal efficiencies herein calculated, four compounds obtained removal rates above 50% (4MBC, BP3, BMDDBM, OC) and the other compounds (HMS, DTS, IMC, MBP) had more variable removal rates (17–100%) after secondary treatment. Removal capacity of WWTPs to eliminate UV filters from water and sludge at some extent strongly depends on the technology implemented in the WWTP and the physicochemical properties of the compounds. It is expected that UV filters can be removed from the water line by sorption onto sludge. Compounds with low water solubility and high log K_{ow} are especially prone to this phenomenon.

3.7. Organic UV filters environmental hazard assessment

The HQs for the measured target organic UV filters in seawater are presented in Table 4. The hazard classification is based on the Hernando et al. criteria (Hernando et al., 2006), where $HQ < 0.01$ corresponds to an unlikely hazard, and an HQ between 0.01 and < 0.1 poses a low hazard, an HQ between 0.1 and < 1 denotes a medium hazard and an $HQ > 1$ indicates a potential high hazard. This classification is pointed out without asterisks (*) for unlikely and low hazard, one asterisk for a medium hazard and two asterisks for a high hazard in Table 4.

According to these results, OC had HQs higher than 1 in all the locations where it was measured (SL1 and SL3), which indicates a high

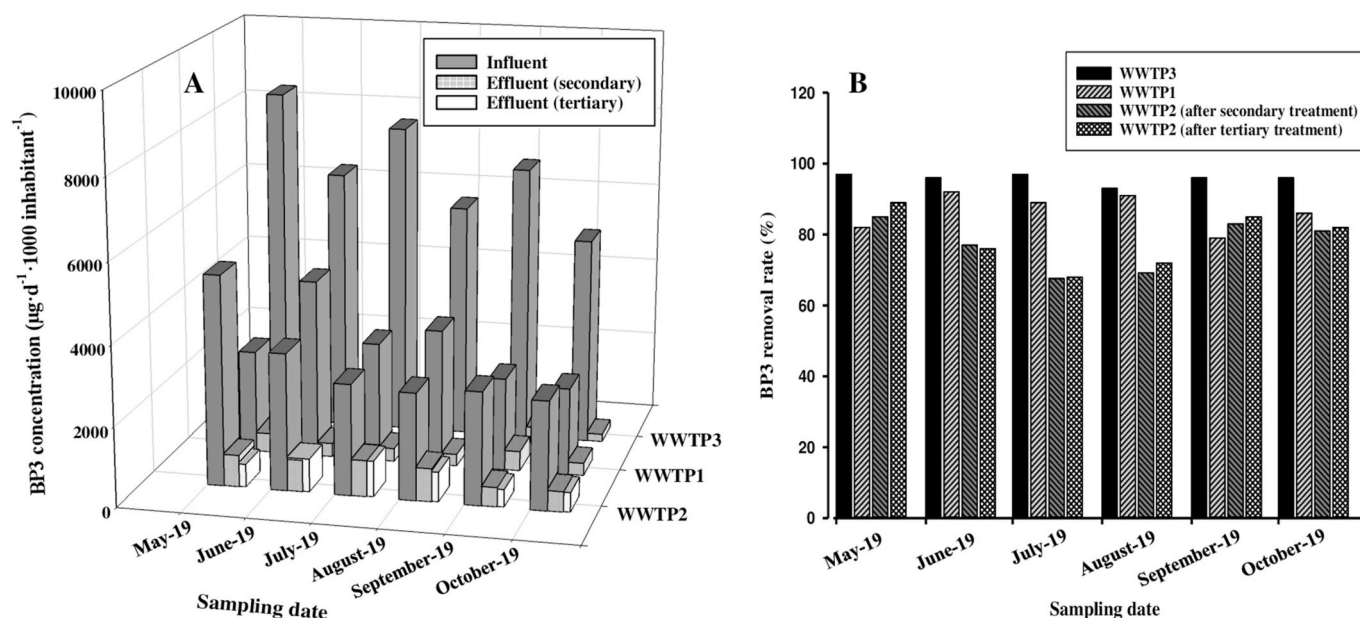


Fig. 3. A: standardized concentration of BP3 in wastewater for the three studied WWTPs. B: removal rates of BP3 in the three WWTPs.

Table 4
Harmful data and HQ values for target UV filters in seawater samples.

Compound	Sampling place	MEC ($\mu\text{g}\cdot\text{L}^{-1}$)			Species	Organism type	EC ₅₀ /LC ₅₀	NOEC	PNEC	HQ ^a		
		Pre-summer	Summer	Post-summer						Pre-summer	Summer	Post-summer
OC	SL 1	–	172 ± 11.4	5.64 ± 0.85	<i>Isochrysis galbana</i> ^a	Microalgae	>150	40	0.8	–	215 ± 14.3**	7.05 ± 1.06**
					<i>Mytilus galloprovincialis</i> ^a	Mussel	>650	20	0.4	430 ± 28.5**	14.1 ± 2.13**	
					<i>Paracentrotus lividus</i> ^a	Sea urchin	737	20	0.4	430 ± 28.5**	14.1 ± 2.13**	
					<i>Isochrysis galbana</i> ^a	Microalgae	>150	40	0.8	3.15 ± 0.33**	–	
	SL 3	–	2.52 ± 0.26	–	<i>Mytilus galloprovincialis</i> ^a	Mussel	>650	20	0.4	–	6.3 ± 0.65**	–
					<i>Paracentrotus lividus</i> ^a	Sea urchin	737	20	0.4	6.3 ± 0.65**	–	
					<i>Isochrysis galbana</i> ^b	Microalga	171.45	18	0.36	48.6 ± 4.72**	–	
					<i>Mytilus galloprovincialis</i> ^b	Mussel	587.17	300	6	2.92 ± 0.28**	–	
4MBC	SL 1	–	17.5 ± 1.70	–	<i>Paracentrotus lividus</i> ^b	Sea urchin	853.74	300	6	–	2.92 ± 0.28**	–
					<i>Siriella armata</i> ^b	Crustacean	192.63	37.04	0.74	23.7 ± 2.30**	–	
					<i>Solea senegalensis</i> ^c	Flatfish malformation	372	235	4.7	3.72 ± 0.36**	–	
						Flatfish length	–	229	4.58	3.82 ± 0.37**	–	
						Flatfish behaviour	–	68	1.36	12.9 ± 1.25**	–	
						Flatfish mortality	439	–	8.78	1.99 ± 0.19**	–	
					<i>Ruditapes philippinarum</i> ^d	Clam	/7.71	–	0.154	113.5 ± 11.0**	–	
					<i>Tigriopus japonicus</i> ^e	Copepod	–	0.5	0.01	1750 ± 170**	–	
	SL 2	–	3.08 ± 0.54	–	<i>Isochrysis galbana</i> ^b	Microalga	171.45	18	0.36	–	8.56 ± 1.50**	–
					<i>Mytilus galloprovincialis</i> ^b	Mussel	587.17	300	6	0.51 ± 0.09*	–	
					<i>Paracentrotus lividus</i> ^b	Sea urchin	853.74	300	6	0.51 ± 0.09*	–	
					<i>Siriella armata</i> ^b	Crustacean	192.63	37.04	0.74	4.16 ± 0.73**	–	
					<i>Solea senegalensis</i> ^c	Flatfish malformation	372	235	4.7	0.66 ± 0.11*	–	
						Flatfish length	–	229	4.58	0.67 ± 0.12*	–	
						Flatfish behaviour	–	68	1.36	2.27 ± 0.40**	–	
						Flatfish mortality	439	–	8.78	0.35 ± 0.06*	–	
BP3	SL 1	0.42 ± 0.06	12.7 ± 9.11	3.43 ± 3.48	<i>Photobacterium phosphoreum</i> ^f	Bacterium	14 270	–	285.4	0.001 ± 0.0002	0.04 ± 0.03	0.01 ± 0.01
					<i>Skeletonema pseudocostatum</i> ^g	Diatom	250	–	5	0.08 ± 0.01	2.53 ± 1.82**	0.69 ± 0.70*
					<i>Isochrysis galbana</i> ^b	Microalgae	13.87	30	0.6	0.70 ± 0.10*	21.1 ± 15.2**	5.72 ± 5.80**
					<i>Mytilus galloprovincialis</i> ^b	Mussel	3472.59	30	0.6	0.70 ± 0.10*	21.1 ± 15.2**	5.72 ± 5.80**
					<i>Paracentrotus lividus</i> ^b	Sea urchin	3280	1920	38.4	0.01 ± 0.002	0.33 ± 0.24*	0.09 ± 0.09
					<i>Siriella armata</i> ^b	Crustacean	710.76	375	7.5	0.06 ± 0.01	1.69 ± 1.21**	0.46 ± 0.46*
					<i>Photobacterium phosphoreum</i> ^f	Bacterium	14 270	–	285.4	0.001 ± 0.0002	0.01 ± 0.0005	0.003 ± 0.002
					<i>Skeletonema pseudocostatum</i> ^g	Diatom	250	–	5	0.04 ± 0.01	0.31 ± 0.03*	0.19 ± 0.11*
	SL 2	0.22 ± 0.07	1.55 ± 0.14	0.97 ± 0.57	<i>Isochrysis galbana</i> ^b	Microalgae	13.87	30	0.6	0.36 ± 0.12*	2.58 ± 0.23**	1.62 ± 0.95**
						Mussel	3472.59	30	0.6	–	–	

(continued on next page)

Table 4 (continued)

Compound	Sampling place	MEC ($\mu\text{g}\cdot\text{L}^{-1}$)			Species	Organism type	EC ₅₀ /LC ₅₀	NOEC	PNEC	HQ ^b		
		Pre-summer	Summer	Post-summer						Pre-summer	Summer	Post-summer
					<i>Mytilus galloprovincialis</i> ^b				0.36 ± 0.12*	2.58 ± 0.23**	1.62 ± 0.95**	
					<i>Paracentrotus lividus</i> ^b	Sea urchin	3280	1920	38.4	0.01 ± 0.002	0.04 ± 0.004	0.03 ± 0.01
					<i>Siriella armata</i> ^b	Crustacean	710.76	375	7.5	0.03 ± 0.01	0.21 ± 0.02*	0.13 ± 0.08*
	SL3	0.17 ± 0.02	4.25 ± 2.14	5.45 ± 3.30	<i>Photobacterium phosphoreum</i> ^f	Bacterium	14 270	–	285.4	0.001 ± 0.0001	0.01 ± 0.01	0.02 ± 0.01
					<i>Skeletonema pseudocostatum</i> ^g	Diatom	250	–	5	0.03 ± 0.004	0.85 ± 0.43*	1.09 ± 0.66**
					<i>Isochrysis galbana</i> ^b	Microalgae	13.87	30	0.6	0.28 ± 0.03*	7.08 ± 3.57**	9.08 ± 5.50**
					<i>Mytilus galloprovincialis</i> ^b	Mussel	3472.59	30	0.6	0.28 ± 0.03*	7.08 ± 3.57**	9.08 ± 5.50**
					<i>Paracentrotus lividus</i> ^b	Sea urchin	3280	1920	38.4	0.004 ± 0.001	0.11 ± 0.06*	0.14 ± 0.09*
					<i>Siriella armata</i> ^b	Crustacean	710.76	375	7.5	0.02 ± 0.003	0.57 ± 0.29*	0.73 ± 0.44*

^a Data from Giraldo et al. (2017)

^b Data from Paredes et al. (2014).

^c Data from Araújo et al. (2018).

^d Data from Santonocito et al. (2020).

^e Data from Chen et al. (2018).

^f Data from Liu et al. (2015).

^g Data from Petersen et al. (2014).

^h Based on the Hernando et al. (2006) risk criteria. No asterisk (*) means unlikely and low risk, one asterisk means medium risk and two asterisk means high risk.

hazard for marine species. For 4MBC, the HQs presented a medium to very high hazard for species depending on sampling places/period, where a higher hazard was found for both copepod and clam.

The calculated HQs for BP3, which was found at all the sampling locations, showed wide variation. In general, medium and high hazard were obtained for this compound in summer, which could be related to the extensive use of sunscreens.

The environmental hazard for 4MBC and BP3 has already been reported on beaches on the Gran Canaria island, but a fresh water crustacean (*Daphnia magna*) and an AF value of 1000 were used to calculate the HQs (Sánchez Rodríguez et al., 2015). The study of Sánchez-Rodríguez et al. found a high hazard for 4MBC (HQ > 2.7) at SL1, which agrees with the HQs stated in this study.

4. Conclusions

Knowledge of the presence of UV filters in seawater and wastewater is very limited. An analytical SPE-UHPLC-MS/MS method for the quantitative analysis of eight widely used organic UV filters was successfully applied to the samples taken on beaches and three WWTPs from the Gran Canaria Island, during a 6-month sampling period in 2019.

Despite the Gran Canaria Island beaches being used almost all year round, the three studied beaches showed seasonal variation for the occurrence of the target organic UV filters, with the highest concentrations in summer than for the pre-summer and post-summer periods. All the analysed seawater samples presented at least one target compound throughout the sampling period. BP-3) was detected in 83% of the samples and the highest concentration was found for OC (172 $\mu\text{g}\cdot\text{L}^{-1}$). The differences between the kind of organic UV filter found and the observed concentrations seems to indicate that accumulation in seawater depends not only on the user type, but also on the water removal ratio, the season and the geomorphological characteristics of the sampling place.

At the studied WWTPs, OC (12 327 $\mu\text{g}\cdot\text{d}^{-1}\cdot 1000\text{ inhabitants}^{-1}$) presented the highest mass load in all the influent samples. BP-3 and

BMDBM were detected in all the influents and secondary treatment effluent throughout the sampling period. BMDBM obtained the widest elimination efficiencies range (83–99%) followed by OC (50–100%). As some compounds are not completely removed during wastewater treatment, they are continuously released to the environment.

Likewise, and comparing the results obtained for beaches with those from secondary effluent, the direct input appears to be the most important source of such pollutants. Even though the secondary wastewater releases from WWTP3 contained the maximum MBP concentration, this compound was not detected in any seawater sample. This could be explained by dilution and its high lipophilicity, which could avoid the transport to beach by currents.

The hazard quotients associated with the measured concentrations showed a potential hazard for the marine species in all the locations where OC was found, while BMDBM presented a medium-high hazard and BP-3 showed widely varying values.

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Author statement

M. Isabel Cadena-Aizaga: Methodology, Validation; Formal analysis; Investigation; Data curation; Writing – original draft. **Sarah Montesdeoca-Esponda:** Conceptualization; Validation; Visualization; Writing – review & editing; Supervision. **Zoraida Sosa-Ferrera:** Conceptualization; Writing – review & editing; Supervision; Resources; Funding acquisition. **José Juan Santana-Rodríguez:** Writing – review & editing; Resources; Funding acquisition.

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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Appendix A. Supplementary data

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References

- Alonso, I., Montesdeoca, I., Vivares, A., Alcántara-Carrió, J., 2001. Variabilidad granulométrica y de la línea de costa en las playas de El Inglés y Maspalomas (Gran Canaria). *Geotemas*, pp. 39–42.
- Araújo, M.J., Rocha, R.J.M., Soares, A.M.V.M., Benedé, J.L., Chisvert, A., Monteiro, M.S., 2018. Effects of UV filter 4-methylbenzylidene camphor during early development of *Solea senegalensis* Kaup, 1858. *Sci. Total Environ.* 628, 1395–1404. <https://doi.org/10.1016/j.scitotenv.2018.02.112>.
- Balmer, M.E., Buser, H.R., Müller, M.D., Poiger, T., 2005. Occurrence of some organic UV filters in wastewater, in surface waters, and in fish from Swiss lakes. *Environ. Sci. Technol.* 39, 953–962. <https://doi.org/10.1021/es040055r>.
- Cadena-Aizaga, M.I., Montesdeoca-Esponda, S., Torres-Padrón, M.E., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2020. Organic UV filters in marine environments: an update of analytical methodologies, occurrence and distribution. *Trends Environ. Anal. Chem.* 25, e00079. <https://doi.org/10.1016/j.teac.2019.e00079>.
- Carve, M., Nugegoda, D., Allinson, G., Shimeta, J., 2021. A systematic review and ecological risk assessment for organic ultraviolet filters in aquatic environments. *Environ. Pollut.* 268, 115894. <https://doi.org/10.1016/j.envpol.2020.115894>.
- Chen, L., Li, X., Hong, H., Shi, D., 2018. Multigenerational effects of 4-methylbenzylidene camphor (4-MBC) on the survival, development and reproduction of the marine copepod *Tigriopus japonicus*. *Aquat. Toxicol.* 194, 94–102. <https://doi.org/10.1016/j.aquatox.2017.11.008>.
- Chisvert, A., Benedé, J.L., Anderson, J.L., Pierson, S.A., Salvador, A., 2017. Introducing a new and rapid microextraction approach based on magnetic ionic liquids: stir bar dispersive liquid microextraction. *Anal. Chim. Acta* 983, 130–140. <https://doi.org/10.1016/j.aca.2017.06.024>.
- Commission, E., 2003. Technical guidance document on risk assessment in support of commission directive 93/67/EEC on risk assessment for new notified substances, commission regulation (EC) No 1488/94 on risk assessment for existing substances, and directive 98/8/EC of the Euro. *Ispra Eur. Comm. Jt. Res. Centre. EUR.* 20418.
- Cunha, S.C., Pena, A., Fernandes, J.O., 2015. Dispersive liquid-liquid microextraction followed by microwave-assisted silylation and gas chromatography-mass spectrometry analysis for simultaneous trace quantification of bisphenol A and 13 ultraviolet filters in wastewaters. *J. Chromatogr., A* 1414, 10–21. <https://doi.org/10.1016/j.chroma.2015.07.099>.
- Danovaro, R., Bongiorno, L., Corinaldesi, C., Giovannelli, D., Damiani, E., Astolfi, P., Greci, L., Pusceddu, A., 2008. Sunscreens cause coral bleaching by promoting viral infections. *Environ. Health Perspect.* 116, 441–447. <https://doi.org/10.1289/ehp.10966>.
- Gobierno de Canarias, Pilotaje del Litoral canario. (n.d.). <https://www.pilotajelitoralcanario.es/#> (accessed January 28, 2021).
- G.C.P. de Turismo, Estadísticas - Web Oficial de Turismo de Gran Canaria, (n.d.). <https://www.grancanaria.com/turismo/area-profesional/informes-y-estadisticas/estadisticas> (accessed January 28, 2021).
- Díaz-Cruz, M.S., Gago-Ferrero, P., Llorca, M., Barceló, D., 2012. Analysis of UV filters in tap water and other clean waters in Spain. *Anal. Bioanal. Chem.* 402, 2325–2333. <https://doi.org/10.1007/s00216-011-5560-8>.
- Downs, C.A., Kramarsky-Winter, E., Segal, R., Fauth, J., Knutson, S., Bronstein, O., Ciner, F.R., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Cadenas, K., Kushmaro, A., Loya, Y., 2016. Toxicopathological effects of the sunscreen UV filter, oxybenzone (Benzophenone-3), on coral planulae and cultured primary cells and its environmental contamination in Hawaii and the U.S. Virgin Islands. *Arch. Environ. Contam. Toxicol.* 70, 265–288. <https://doi.org/10.1007/s00244-015-0227-7>.
- EC, 2009. Regulation (EC) No 1223/2009 of the European parliament and of the council of 30 november 2009 on cosmetic products. *Off. J. Eur. Union L342* 52, 59–209.
- Emmanouil, C., Bekyrou, M., Psomopoulos, C., Kungolos, A., 2019. An insight into ingredients of toxicological interest in personal care products and a small-scale sampling survey of the Greek market: delineating a potential contamination source for water resources. *Water* 11, 2501. <https://doi.org/10.3390/w11122501>.
- Fagervold, S.K., Rodrigues, A.S., Rohée, C., Roe, R., Bourrain, M., Stien, D., Lebaron, P., 2019. Occurrence and environmental distribution of 5 UV filters during the summer season in different water bodies. *Water. Air Soil Pollut.* 230, 1–13. <https://doi.org/10.1007/s11270-019-4217-7>.
- Fivenson, D., Sabzevari, N., Qiblawi, S., Blitz, J., Norton, B.B., Norton, S.A., 2020. Sunscreens: UV filters to protect us: Part 2-Increasing awareness of UV filters and their potential toxicities to us and our environment. *Int. J. Women's Dermatol.* 7, 45–69. <https://doi.org/10.1016/j.ijwd.2020.08.008>.
- Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2013a. Liquid chromatography-tandem mass spectrometry for the multi-residue analysis of organic UV filters and their transformation products in the aquatic environment. *Anal. Methods* 5, 355–366. <https://doi.org/10.1039/c2ay26115d>.
- Gago-Ferrero, P., Mastroianni, N., Díaz-Cruz, M.S., Barceló, D., 2013b. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction-liquid chromatography-tandem mass spectrometry. *J. Chromatogr., A* 1294, 106–116. <https://doi.org/10.1016/j.chroma.2013.04.037>.
- García-Guerra, R.B., Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Kabir, A., Furton, K.G., Santana-Rodríguez, J.J., 2016. Rapid monitoring of residual UV-stabilizers in seawater samples from beaches using fabric phase sorptive extraction and UHPLC-MS/MS. *Chemosphere* 164, 201–207. <https://doi.org/10.1016/j.chemosphere.2016.08.102>.
- Giokas, D.L., Salvador, A., Chisvert, A., 2007. UV filters: from sunscreens to human body and the environment. *TrAC Trends Anal. Chem. (Reference Ed.)* 26, 360–374. <https://doi.org/10.1016/j.trac.2007.02.012>.
- Giraldo, A., Montes, R., Rodil, R., Quintana, J.B., Vidal-Liñán, L., Beiras, R., 2017. Ecotoxicological evaluation of the UV filters Ethylhexyl dimethyl p-aminobenzoic acid and Octocrylene using marine organisms *Ischrysis galbana*, *Mytilus galloprovincialis* and *Paracentrotus lividus*. *Arch. Environ. Contam. Toxicol.* 72, 606–611. <https://doi.org/10.1007/s00244-017-0399-4>.
- Goksøyr, A., Tollefsen, K.E., Grung, M., Løken, K., Lie, E., Zenker, A., Fent, K., Schlabach, M., Huber, S., 2009. Balsa raft crossing the pacific finds low contaminant levels. *Environ. Sci. Technol.* 43, 4783–4790. <https://doi.org/10.1021/es900154h>.
- Hernando, M.D., Mezcuá, M., Fernández-Alba, A.R., Barceló, D., 2006. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta* 69, 334–342. <https://doi.org/10.1016/j.talanta.2005.09.037>.
- Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J., 2009. The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. *Water Res.* 43, 363–380. <https://doi.org/10.1016/j.watres.2008.10.047>.
- Kupper, T., Plagellat, C., Brändli, R.C., de Alencastro, L.F., Grandjean, D., Tarradellas, J., 2006. Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment. *Water Res.* 40, 2603–2612. <https://doi.org/10.1016/j.watres.2006.04.012>.
- Li, W.L., Zhang, Z.F., Ma, W.L., Liu, L.Y., Song, W.W., Li, Y.F., 2018. An evaluation on the intra-day dynamics, seasonal variations and removal of selected pharmaceuticals and personal care products from urban wastewater treatment plants. *Sci. Total Environ.* 640, 1139–1147. <https://doi.org/10.1016/j.scitotenv.2018.05.362>.
- Liu, H., Sun, P., Liu, H., Yang, S., Wang, L., Wang, Z., 2015. Acute toxicity of benzophenone-type UV filters for *Photobacterium phosphoreum* and *Daphnia magna*: QSAR analysis, interspecies relationship and integrated assessment. *Chemosphere* 135, 182–188. <https://doi.org/10.1016/j.chemosphere.2015.04.036>.
- Magi, E., Scapolla, C., Di Carro, M., Rivaro, P., Ngoc Nguyen, K.T., 2013. Emerging pollutants in aquatic environments: monitoring of UV filters in urban wastewater treatment plants. *Anal. Methods* 5, 428–433. <https://doi.org/10.1039/c2ay26163d>.
- McKnight, L., Rodríguez, G., 2017. Distribution of marine debris stranded on a city beach: a case study of Las Canteras Beach, Gran Canaria. In: *Coastal Cities and Their Sustainable Future II*, p. 11. <https://doi.org/10.2495/CC170021>.
- Molins-Delgado, D., Díaz-Cruz, M.S., Barceló, D., 2014. Introduction: personal care products in the aquatic environment. In: *Personal Care Products in the Aquatic Environment*, pp. 1–34. <https://doi.org/10.1007/978-2014-302>.
- Molins-Delgado, D., Muñoz, R., Nogueira, S., Alonso, M.B., Torres, J.P., Malm, O., Zioli, R.L., Hauser-Davis, R.A., Eljarrat, E., Barceló, D., Díaz-Cruz, M.S., 2018. Occurrence of organic UV filters and metabolites in lebranche mullet (*Mugil liza*) from Brazil. *Sci. Total Environ.* 618, 451–459. <https://doi.org/10.1016/j.scitotenv.2017.11.033>.
- Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2012. On-line solid-phase extraction coupled to ultra-performance liquid chromatography with tandem mass spectrometry detection for the determination of benzotriazole UV stabilizers in coastal marine and wastewater samples. *Anal. Bioanal. Chem.* 403, 867–876. <https://doi.org/10.1007/s00216-012-5906-x>.
- Montesdeoca-Esponda, S., Del Toro-Moreno, A., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2013. Development of a sensitive determination method for benzotriazole UV stabilizers in environmental water samples with stir bar sorption extraction and liquid desorption prior to ultra-high performance liquid chromatography with tandem mass spectrometry. *J. Separ. Sci.* 36, 2168–2175. <https://doi.org/10.1002/jssc.201300191>.
- Montesdeoca-Esponda, S., Álvarez-Raya, C., Torres-Padrón, M.E., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2019. Monitoring and environmental risk assessment of benzotriazole UV stabilizers in the sewage and coastal environment of Gran Canaria (Canary Islands, Spain). *J. Environ. Manag.* 233, 567–575. <https://doi.org/10.1016/j.jenvman.2018.12.079>.
- Montesdeoca-Esponda, S., Torres-Padrón, M.E., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2021. Fate and distribution of benzotriazole UV filters and stabilizers in environmental compartments from Gran Canaria Island (Spain): a comparison study. *Sci. Total Environ.* 756, 144086. <https://doi.org/10.1016/j.scitotenv.2020.144086>.
- Nouri, N., Khorram, P., Duman, O., Sibel, T., Hassan, S., 2020. Overview of nanosorbents used in solid phase extraction techniques for the monitoring of emerging organic contaminants in water and wastewater samples. *Trends Environ. Anal. Chem.* 20, e00081. <https://doi.org/10.1016/j.teac.2020.e00081>.
- Paredes, E., Perez, S., Rodil, R., Quintana, J.B., Beiras, R., 2014. Ecotoxicological evaluation of four UV filters using marine organisms from different trophic levels *Ischrysis galbana*, *Mytilus galloprovincialis*, *Paracentrotus lividus*, and *Siriella armata*. *Chemosphere* 104, 44–50. <https://doi.org/10.1016/j.chemosphere.2013.10.053>.

- Peng, X., Jin, J., Wang, C., Ou, W., Tang, C., 2015. Multi-target determination of organic ultraviolet absorbents in organism tissues by ultrasonic assisted extraction and ultra-high performance liquid chromatography-tandem mass spectrometry. *J. Chromatogr., A* 1384, 97–106. <https://doi.org/10.1016/j.chroma.2015.01.051>.
- Perez-Torrado, F.-J., Mangas, J., 1994. Origen y evolución geológica de la barra de Las Canteras (Las Palmas de Gran Canaria). *Vector* 1, 4–13.
- Petersen, K., Heiaas, H.H., Tollefsen, K.E., 2014. Combined effects of pharmaceuticals, personal care products, biocides and organic contaminants on the growth of *Skeletonema pseudocostatum*. *Aquat. Toxicol.* 150, 45–54. <https://doi.org/10.1016/j.aquatox.2014.02.013>.
- Ramos, S., Homem, V., Alves, A., Santos, L., 2015. Advances in analytical methods and occurrence of organic UV-filters in the environment - a review. *Sci. Total Environ.* 526, 278–311. <https://doi.org/10.1016/j.scitotenv.2015.04.055>.
- Ramos, S., Homem, V., Alves, A., Santos, L., 2016. A review of organic UV-filters in wastewater treatment plants. *Environ. Int.* 86, 24–44. <https://doi.org/10.1016/j.envint.2015.10.004>.
- Ramos, S., Homem, V., Santos, L., 2019. Simultaneous determination of synthetic musks and UV-filters in water matrices by dispersive liquid-liquid microextraction followed by gas chromatography tandem mass-spectrometry. *J. Chromatogr., A* 1590, 47–57. <https://doi.org/10.1016/j.chroma.2019.01.013>.
- Ramos, S., Homem, V., Santos, L., 2020. Analytical methodology to screen UV-filters and synthetic musk compounds in market tomatoes. *Chemosphere* 238, 124605. <https://doi.org/10.1016/j.chemosphere.2019.124605>.
- Sánchez Rodríguez, A., Rodrigo Sanz, M., Betancort Rodríguez, J.R., 2015. Occurrence of eight UV filters in beaches of Gran Canaria (Canary Islands). An approach to environmental risk assessment. *Chemosphere* 131, 85–90. <https://doi.org/10.1016/j.chemosphere.2015.02.054>.
- Sánchez-Brunete, C., Miguel, E., Albero, B., Tadeo, J.L., 2011. Analysis of salicylate and benzophenone-type UV filters in soils and sediments by simultaneous extraction cleanup and gas chromatography-mass spectrometry. *J. Chromatogr., A* 1218, 4291–4298. <https://doi.org/10.1016/j.chroma.2011.05.030>.
- Santonocito, M., Salerno, B., Trombini, C., Tonini, F., Pintado-Herrera, M.G., Martínez-Rodríguez, G., Blasco, J., Lara-Martín, P.A., Hampel, M., 2020. Stress under the sun: effects of exposure to low concentrations of UV-filter 4-methylbenzylidene camphor (4-MBC) in a marine bivalve filter feeder, the Manila clam *Ruditapes philippinarum*. *Aquat. Toxicol.* 221, 105418. <https://doi.org/10.1016/j.aquatox.2020.105418>.
- Santos, A.J.M., Miranda, M.S., Esteves da Silva, J.C.G., 2012. The degradation products of UV filters in aqueous and chlorinated aqueous solutions. *Water Res.* 46, 3167–3176. <https://doi.org/10.1016/j.watres.2012.03.057>.
- Schmitt, C., Oetken, M., Dittberner, O., Wagner, M., Oehlmann, J., 2008. Endocrine modulation and toxic effects of two commonly used UV screens on the aquatic invertebrates *Potamopyrgus antipodarum* and *Lumbriculus variegatus*. *Environ. Pollut.* 152, 322–329. <https://doi.org/10.1016/j.envpol.2007.06.031>.
- Sereshti, H., Duman, O., Tunç, S., Nouri, N., Khorram, P., 2020. Nanosorbent-based solid phase microextraction techniques for the monitoring of emerging organic contaminants in water and wastewater samples. *Microchim. Acta* 187, 1–35. <https://doi.org/10.1007/s00604-020-04527-w>.
- Tarazona, I., Chisvert, A., León, Z., Salvador, A., 2010. Determination of hydroxylated benzophenone UV filters in sea water samples by dispersive liquid-liquid microextraction followed by gas chromatography-mass spectrometry. *J. Chromatogr., A* 1217, 4771–4778. <https://doi.org/10.1016/j.chroma.2010.05.047>.
- Tovar-Sánchez, A., Sánchez-Quiles, D., Basterretxea, G., Benedé, J.L., Chisvert, A., Salvador, A., Moreno-Garrido, I., Blasco, J., 2013. Sunscreen products as emerging pollutants to coastal waters. *PLoS One* 8, e65451. <https://doi.org/10.1371/journal.pone.0065451>.
- Tsui, M.M.P., Leung, H.W., Wai, T.C., Yamashita, N., Taniyasu, S., Liu, W., Lam, P.K.S., Murphy, M.B., 2014a. Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries. *Water Res.* 67, 55–65. <https://doi.org/10.1016/j.watres.2014.09.013>.
- Tsui, M.M.P., Leung, H.W., Lam, P.K.S., Murphy, M.B., 2014b. Seasonal occurrence, removal efficiencies and preliminary risk assessment of multiple classes of organic UV filters in wastewater treatment plants. *Water Res.* 53, 58–67. <https://doi.org/10.1016/j.watres.2014.01.014>.
- Vila, M., Pablo Lamas, J., Garcia-Jares, C., Dagnac, T., Llopart, M., 2016a. Ultrasound-assisted emulsification microextraction followed by gas chromatography-mass spectrometry and gas chromatography-tandem mass spectrometry for the analysis of UV filters in water. *Microchem. J.* 124, 530–539. <https://doi.org/10.1016/j.microc.2015.09.023>.
- Vila, M., Celeiro, M., Lamas, J.P., Dagnac, T., Llopart, M., Garcia-Jares, C., 2016b. Determination of fourteen UV filters in bathing water by headspace solid-phase microextraction and gas chromatography-tandem mass spectrometry. *Anal. Methods* 8, 7069–7079. <https://doi.org/10.1039/c6ay01787h>.
- Vila, M., Celeiro, M., Lamas, J.P., Garcia-Jares, C., Dagnac, T., Llopart, M., 2017. Simultaneous in-vial acetylation solid-phase microextraction followed by gas chromatography tandem mass spectrometry for the analysis of multiclass organic UV filters in water. *J. Hazard Mater.* 323, 45–55. <https://doi.org/10.1016/j.jhazmat.2016.06.056>.
- Zhong, X., Downs, C.A., Li, Y., Zhang, Z., Li, Y., Liu, B., Gao, H., Li, Q., 2020. Comparison of toxicological effects of oxybenzone, avobenzene, octocrylene, and octinoxate sunscreen ingredients on cucumber plants (*Cucumis sativus* L.). *Sci. Total Environ.* 714, 136879. <https://doi.org/10.1016/j.scitotenv.2020.136879>.