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Occurrence and ecological risk assessment of organic UV filters in coastal waters of the Iberian Peninsula

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ABSTRACT

This study aimed to assess the presence of 21 UVFs and metabolites in coastal regions of the Iberian Peninsula, to evaluate their environmental risk, and identify possible influential factors affecting their measured concentrations. Sampling was carried out in spring and summer to assess possible seasonal variations. UVFs were detected in 43 of the 46 sampling sites. Only 5 were found above LOD: BP4, OC, BP3 and metabolites BP1 and BP8. Samples collected in Mar Menor had the greatest variety of compounds per sample and the highest cumulative concentrations. The risk was characterized using Risk Quotients (RQ). BP1 showed a Low environmental Risk in 2 sites while for OC the RQ indicated a Moderate Risk in 22 points. The variables that contribute most to the variation are population density, sampling season, whether it was an open bay or not, and level of urbanization. The presence of WWTPs had a lower influence.

Abbreviations: AF, Assessment Factor; BP1, Benzophenone-1; BP3, Oxybenzone (Benzophenone-3); BP4, Sulisobenzone (Benzophenone-4); BP8 (DHMB), Dioxybenzone (Benzophenone-8); EU, European Union; L(*E*)C50, Mean (or effective) Lethal Concentration; LOEC, Lowest Effect Concentration; LOD, Limit of detection; LOQ, Limit of quantification; MEC, Measured environmental concentration; NOEC, No Observed Effect Concentrations; OC, Octocrylene; PCPs, Personal care products; PEC, Predicted environmental concentration; PNEC, Predicted no-effect concentration; RQ, Risk Quotient; SPE, Solid phase extraction; UVFs, UV filters; WWTPs, Wastewater Treatment PlantsRDA - Redundancy Analysis; LCL, Lower Confidence Level.

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1. Introduction

UV (ultraviolet) filters (UVFs) are substances used to block solar UV radiation and are part of personal care products (PCPs), such as sunscreens or cosmetics, as well as some industrial products. These compounds have been increasingly used in recent decades due to growing concerns about the adverse effects of UV radiation on various skin diseases (Fenni et al., 2022; Tovar-Sánchez et al., 2013; Mustieles et al., 2023). In the EU, these substances are registered according to the risk assessment procedures established by the European Agency for Chemicals (ECHA) and are classified as cosmetic substances (Directive 76/768/EEC and subsequent amendments) included in Annex VI of Regulation (EC) 1223/2009. To date, it has been considered that the toxic effects that these substances may have on the environment are outweighed by the benefits they provide for human health in reducing the deleterious effects of overexposure to UV radiation (NASEM, 2022).

UVFs have been detected in different environmental matrices in aquatic systems, including water, sediments, and biota (Fenni et al., 2022; Gago-Ferrero et al., 2012; Gago-Ferrero et al., 2013; He et al., 2019; Molins-Delgado et al., 2016b; Langford et al., 2015; Pawlowski et al., 2019). They are considered emerging and persistent pollutants in aquatic ecosystems due to their physicochemical properties and their extensive and (semi-)continuous release (Campos et al., 2017b; Gasco Cavero et al., 2023; Huang et al., 2021; Molins-Delgado et al., 2016b; Pintado-Herrera et al., 2017). It is believed that their environmental release is primarily caused by direct inputs from human skin washing in recreational areas or by WWTP discharges given that they are hardly removed by conventional treatments (Apel et al., 2018; Bell et al., 2017; Downs et al., 2022a; Fagervold et al., 2021; He et al., 2019; Mitchelmore et al., 2021; Molins-Delgado et al., 2016a; Tsui et al., 2014). Some of them have been considered for decades as endocrine disruptors, affecting the feeding, growth, or reproduction of several species (Campos et al., 2017a; Gago-Ferrero et al., 2012; He et al., 2019; Tsui et al., 2014; Yan et al., 2020). In fact, they are considered as a fundamental factor in coral bleaching due to the effects that some of them have on primary producers such as algae (Downs et al., 2022a; Mitchelmore et al., 2021; Sharifan, 2020).

Numerous studies have highlighted the potential environmental risks posed by UVFs and have reported preliminary risk assessments for different UVFs in aquatic ecosystems (freshwater and marine), using measured environmental concentrations in both sediment and water samples (Pintado-Herrera et al., 2017; Ramos et al., 2015; Sang and Leung, 2016; Tsui et al., 2015). Three of these substances, namely octocrylene, avobenzone, and oxybenzone, have recently been proposed to be included in the 4th Watch List (WL) under the Water Framework Directive (WFD) (Gomez Cortes et al., 2022), indicating a need for additional monitoring data. Despite the increasing focus on monitoring their presence in European surface waters, their toxic effects on aquatic biota are poorly understood. Quantitatively assessing their impact on marine ecosystems is challenging. Many toxicity studies have focused on short-term exposure, while a comprehensive risk assessment should consider chronic toxicity data due to their lipophilic properties, bioaccumulation potential, low biodegradability, and continuous release into the environment (Agawin et al., 2022; NASEM, 2022). Additionally, interactions with other UVFs, metabolites, and environmental factors like climate change may lead to increase their toxicity (NASEM, 2022; Yang et al., 2020; Campos et al., 2017a; Molins-Delgado et al., 2016b). Some authors have highlighted the importance of developing environmental quality standards for UVFs based on toxicity tests with key aquatic organisms, which may help decide whether the current input into the environment should be reduced or not (Campos et al., 2017a; Downs et al., 2022a; Fenni et al., 2022; Mitchelmore et al., 2021; Pintado-Herrera et al., 2017). A recent report by the US National Academies (NASEM, 2022) provided the most complete and up-to-date environmental assessment of common organic and inorganic UVFs.

In marine and coastal ecosystems, their presence is especially concerning due to the influence of WWTP effluents, illegal dumping, or excessive tourist influx (Agawin et al., 2022; Downs et al., 2022a; Mitchelmore et al., 2021; Pintado-Herrera et al., 2017; Tovar-Sánchez et al., 2013). Risk and possible adverse effects in marine ecosystems have also been assessed in several studies (Downs et al., 2022a; Kim et al., 2017; Paredes et al., 2014; Sang and Leung, 2016; Schaap and Slijkerman, 2018; Rodríguez et al., 2015). Also, several studies have found a positive correlation between the concentrations detected in aquatic ecosystems and anthropogenic activities, with many of them identifying recreational activities as the most relevant source of UVFs in coastal areas (Bell et al., 2017; Pintado-Herrera et al., 2017; Sang and Leung, 2016; Schaap and Slijkerman, 2018). Besides the anthropogenic pressure, it is suspected that the geomorphological and hydrological conditions of coastal water bodies are key factors influencing UVF exposure, as the highest concentrations occur in "semi-enclosed" beaches (Downs et al., 2022c; Mitchelmore et al., 2021; Rodríguez et al., 2015). Coastal areas like the Mediterranean, which are subjected to low tidal effects and include semi-enclosed beaches and coastal lagoons with high tourist pressure, may be considered highly vulnerable areas. Much earlier studies already warned about the threat of anthropogenic pollutants in the Mediterranean Sea, a basin greatly affected by urban and industrial discharges from various countries (Sánchez-Ávila et al., 2012). No studies have quantified and evaluated the presence of UVFs on beaches of the Iberian Peninsula, and further studies on their environmental risks are needed, especially if current human occupation trends continue.

To advance the knowledge regarding the impact of the presence of UVFs in coastal aquatic ecosystems of special environmental and tourist interest, the objectives of this study were: (1) to identify and quantify the presence of 21 organic UVFs and metabolites in coastal areas of the Iberian Peninsula, (2) to assess their environmental risk (3) and to analyze which factors may have a greater influence on concentrations detected in marine environments.

2. Materials and methods

2.1. Study sites and sample collection

A total of 46 beaches were sampled within this study. Sixteen beaches were selected along the Portuguese coast, mainly in the Lisbon and Algarve area, with another 30 in two separate areas of the Spanish coast: 18 in the Cádiz-Málaga area and 12 in the coastal saltwater lagoon of Mar Menor (Murcia). Beaches were selected with a wide range of anthropogenic influence and pressures: areas close to natural or protected areas that are less frequented by humans, as well as areas of difficult access, and highly urbanized areas, which have a large tourist influx (Fig. 1). A total of 61 coastal water samples were collected during the spring and/or summer of 2021 to assess seasonal variation in the concentrations of the measured compounds. In May 2021, 17 samples were collected in the Cádiz-Málaga area, and the rest were collected in August 2021: 16 samples in Lisbon-Algarve, 16 in Cádiz-Málaga, and 12 in Mar Menor.

Samples were collected from the upper part of the water column (approximately 20 cm) in opaque 0.5 L PET bottles. On each beach, samples were taken at 3 different points twice a day with a 12-h difference. The composite sample of each beach was obtained by mixing the six samples. All samples were stored refrigerated and, once fieldwork was completed, they were stored at −20 °C until further analysis.

2.1.1. Portugal

On one hand, in Lisbon region, the surveyed beaches were close to protected natural areas, such as the Estuary do Tejo Nature Reserve, located at the mouth of the Tagus River to the Atlantic Ocean, the Sado Estuary, and the Arrábida Natural Park. Despite being difficult to access and having protection measures in place, these beaches have experienced an increasing tourist influx during the summer season. On the

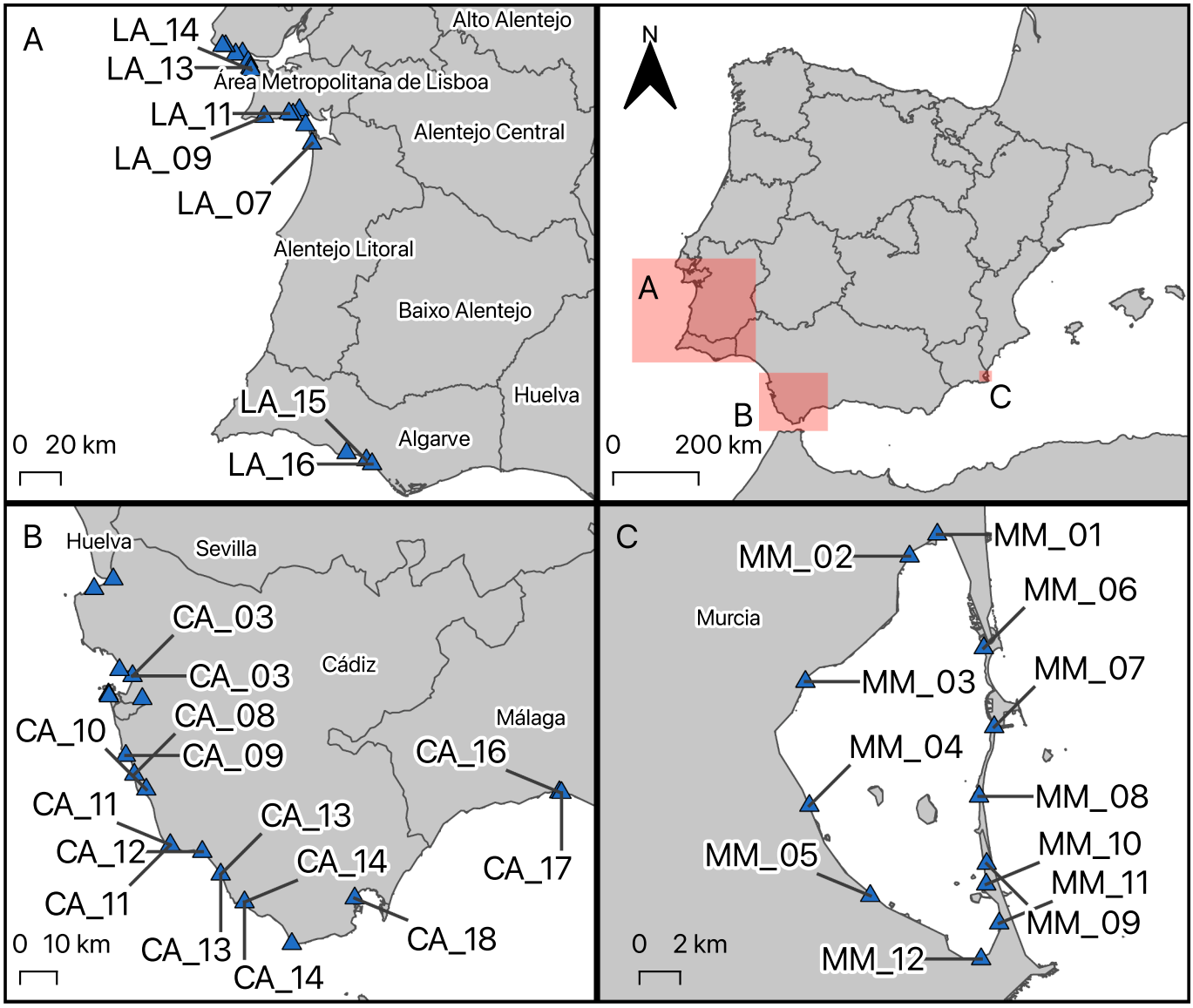

Fig. 1. Iberian Peninsula map with three study areas and detailed maps of specific sampling locations in Lisbon-Algarve (A), Cádiz-Málaga (B), and Mar Menor (C).

other hand, Algarve's beaches were expected to be more populated as there is a large tourist tradition in this area that has increased considerably in recent years.

2.1.2. Spain

In Spain, 14 beaches were sampled along the coast of Cádiz (Atlantic Ocean), in areas close to the Natural Park of the Bay of Cádiz, as well as near ports and other urban areas. Samples were also collected on more dispersed beaches away from the city, at two points at the mouth of the Guadalquivir River and on the beach of Tarifa within the Natural Park of Los Alcornocales, in the Strait of Gibraltar. To the east of the strait, on the coast of the Alboran Sea (Mediterranean Sea), in Málaga, two other samples were collected.

In Mar Menor, 12 sites were sampled, all of them on the interior coast of the lagoon. Mar Menor is the largest saltwater lagoon in Spain and is under national and international environmental protection as SPAMI (Specially Protected Areas of Mediterranean Importance). It also has been included in the Ramsar list since 1994. It is a semi-closed ecosystem, connected to the Mediterranean Sea at its northernmost tip and therefore highly susceptible to human activities and has long been the subject of controversy for illegal dumping of the agricultural industry and untreated wastewater that are leading to the destruction of its native fauna and environmental deterioration. (Álvarez-Rogel et al., 2020; Ruiz-Fernández et al., 2020).

2.2. Chemical analysis

Twenty-one compounds belonging to 8 chemical families of UVFs or UV blockers were included in the analytical method used for this study (Table 1). Sample treatment was carried out at the water quality laboratory of the Madrid Institute for Advanced Studies on water (IMDEA Water). Target compounds were extracted by applying a solid phase extraction (SPE) protocol. Water samples were filtered through a 0.7 μm glass fiber filter and passed through an Oasis HLB SPE cartridge (200 mg, 6 mL), previously conditioned with 6 mL of MeOH, followed by 6 mL of ultrapure water. After loading the sample by gravity, cartridges were rinsed with three aliquots of 10 mL of ultrapure water and dried for 2 min under vacuum (5 bar) to eliminate residual water. Analytes were eluted with three aliquots of 4 mL of MeOH. The extract was evaporated to dryness using a Speed Vac concentrator (ThermoScientific, USA) at 45 °C and 0.2 Torr. Then, extracts were reconstituted in 0.5 mL of MeOH: water, (10:90 %, *v*/v), centrifuged for 5 min at 13000 rpm

Table 1
List of UVFs analyzed and their limit of detection (LOD) and limit of quantitation (LOQ). Compound found above the limit of detection in at least one sample are highlighted with a (*).

Compound ID	CAS num.	Compound	Alternate common name	Group	Family	Metabolite of	LOD (μg/L)	LOQ (μg/L)	Recoveries (%)
4DBH	611-99-4	4,4'-Dihydroxybenzophenone	-	UVF	Benzophenones	-	0.009	0.029	113.1
4HB	1137-42-4	4-Hydroxybenzophenone	-	UVF	Benzophenones	-	0.006	0.021	96.1
4MBC	36861-47-9	4-Methylbenzylidenecamphor	Enzacamene	UVF	Camphors	-	0.011	0.038	114.6
AVO	70356-09-1	Avobenzone	-	UVF	Benzophenones	-	0.010	0.034	91.2
BP	119-61-9	Benzophenone	-	UVF	Benzophenones	Octocrylene	0.005	0.020	98.2
BP1 *	131-56-6	Benzophenone-1	-	UVF	Benzophenones	Benzophenone-3	0.005	0.016	95.2
BP2	131-55-5	Benzophenone-2	-	UVF	Benzophenones	-	0.007	0.024	89.7
BP3 *	131-57-7	Oxybenzone	Benzophenone-3	UVF	Benzophenones	-	0.006	0.019	109.2
BP4 *	4065-45-6	Sulisobenzone	Benzophenone-4	UVF	Benzophenones	-	0.008	0.027	99.0
BZT	95-14-7	Benzotriazole	-	UV blokers	Benzotriazoles	-	0.008	0.028	101.5
DHMB *	131-53-3	Dioxybenzone	Benzophenone-8	UVF	Benzophenones	Benzophenone-3	0.005	0.017	82.0
DMBZT	4184-79-6	Dimethyl-benzotriazole	-	UV blokers	Benzotriazoles	-	0.006	0.019	104.5
EHMC	5466-77-3	Octinoxate	Ethylhexyl methoxycinnamate	UVF	Cinnamates	-	0.006	0.021	112.5
EtPABA	94-09-7	Benzocaine	Ethyl-PABA	UVF	p-Aminobenzoic acid derivatives	-	0.011	0.038	81.5
HMS	118-56-9	Homosalate	-	UVF	Salicylates	-	0.023	0.076	98.1
MeBZT	136-86-5	Methyl-benzotriazole	-	UV blokers	Benzotriazoles	-	0.004	0.013	97.7
OC *	6197-30-4	Octocrylene	-	UVF	Crylenes	-	0.007	0.022	80.0
OTS	118-60-5	Octisalate	Octylsalicylate	UVF	Salicylates	-	0.022	0.073	98.7
UV-234	70321-86-7	UV-234	-	UV blokers	Benzotriazoles	-	0.004	0.012	81.0
UV-329	3147-75-9	Octrizole	UV-329	UV blokers	Benzotriazoles	-	0.015	0.051	105.9
UVP	2440-22-4	Drometrizole	-	UV blokers	Benzotriazoles	-	0.007	0.022	94.4

(MiniSpin centrifuge, Eppendorf, USA), and, finally, transferred to an amber glass vial. SPE extracts were frozen and shipped to the IDAEA-CSIC (Barcelona), where remained frozen until analysis by liquid chromatography coupled to tandem mass spectrometry with a triple quadrupole analyzer (LC-(QqQ)-MS/MS). A Transcend TLX-1 liquid chromatograph coupled to a TSQ mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) was employed for UVFs quantification. The chromatographic separation was carried out using a Purospher® STAR RP-18 ec. column Merck KGaA). All samples were analyzed in two ionization modes: positive and negative, by electrospray ionization (ESI+ and ESI-). It was operated in selected reaction monitoring mode (SRM). To ensure analytical certainty, standard solutions were incorporated into the sequence of samples as quality controls for QA/QC purposes. Likewise, methodological blanks were made throughout the analysis sequences. All compounds were quantified and confirmed with the recording of the 2 most intense SRM transitions. The quantification of the samples was carried out by isotopic dilution using the corresponding marked isotopic standards and the most intense SRM recorded. All analyses were carried out following the EU normative (Commission Decision, 2002/657/EC) in which compounds were identified with the chromatographic retention time (tR) comparing with those of the standards at a maximum tolerance of 2.5 % and that ion intensities between the selected SRM transitions were below 15 %. A detailed description of the analytical methodology applied, and its performance is provided in Gasco Cavero et al. (2023).

2.3. Environmental risk assessment and influencings factors

The environmental risk to the coastal aquatic environment was assessed for those UVFs which were found above LOD in at least one sample. The risk was assessed following a modified Risk Quotient (RQ) approach (also known as Hazard Quotients, or Risk characterization ratios) (ECHA, 2012). Traditionally, RQs are calculated as the ratio of a predicted environmental concentration (PEC) to a PNEC, or the predicted no-effect concentration. PNECs are usually derived by selecting the most reliable toxicity data for the most sensitive species and dividing it by an additional assessment factor (AF) to account for uncertainty associated to data availability and nature (ECHA, 2011). In this study, the assessment was based on measured concentrations and RQs were estimated for each collected sample by dividing the MEC for each compound at each location by a suitable PNEC. An RQ of <0.1 indicates that no adverse effects are to be expected, an RQ between 0.1 and 1 would represent a low risk, between 1 and 10 a moderate risk and above 10 would indicate a high risk.

We decided to follow a precautionary approach by assessing the risk from chronic exposure so PNECs were based on chronic toxicity data. In the case of BP3, sufficient chronic laboratory toxicity data were available to allow for the development of a species sensitivity distribution

(SSD) (NASEM, 2022). As such, for this compound, RQs were calculated by dividing the MEC by the lower limit of the 95 % confidence interval LCL of the HC5 (Concentration at which 5 % of the species in the SSD exhibit an effect), or the concentration which would be hazardous to 5 % of the species. The HC5 and its LCL for the SSD for BP3 presented in the NASEM report were used for these calculations (NASEM, 2022). While this HC5 LCL does not represent a PNEC, it does provide a more realistic estimate of risk and any RQ < 1 (AC $= 1$) calculated this way would imply that effects are expected on >5 % of the species, which is typically considered the cut-off for unacceptable risk in higher tiers of risk assessment. For all other UVFs, relevant databases of toxicological data, such as the US EPA ECOTOX database (US EPA, 2023) or the Enviro Tox database (Connors et al., 2019), as well as the general literature were reviewed for experimental data on typical endpoints (e.g., mortality, growth, reproduction) or specifically relevant endpoints (e.g., coral bleaching) (NASEM, 2022) derived from chronic studies. In the case of BP1, no suitable experimental data was found, and the lowest QSAR-derived Chronic Value (ChV) provided by the US EPA ECOSAR (US EPA, 2017) was used. Table 2 lists the selected effect measured for each compound, AFs used, and final benchmark concentration (PNEC or HC5 LCL).

To determine the influencing factors a redundancy analysis (RDA) was done to assess the influence of different monitoring variables on the concentration of UVFs. This is a statistical method that allows studying the relationship between two tables of variables Y and X. The variables included in the analysis were: the sampling season (spring or summer), tourist influx or population density (low, medium, or high during the sampling time), the presence of a nearby WWTP at <5 km (yes or no), urbanization in the surrounding area (yes or no), and whether the sampling site was in the open sea or not. The RDA analysis was performed with the software Canoco v5.0 (Ter Braak and Šmilauer, 2012) using 999 Monte Carlo permutations. Before the analysis the concentration data was log x + 1 transformed and the concentrations below de LOD were replaced by zeros.

3. Results and discussion

3.1. Occurrence characterization

Out of the 21 UVFs analyzed, only 5 were found above their respective LODs in at least one sample: BP4, OC, BP3 and two of BP3 metabolites BP1 and BP8. SI Table 3 summarizes the detection frequencies for the compounds in the various areas and seasons. BP4 was present in 92 % of the collected samples, followed by OC (36 %) and BP3 (31 %), while both metabolites (BP1 and BP8) were rarely detected (3 %). It is necessary to note at this point the fact of the COVID-19 pandemic, since in the course of the sampling there were mobility restrictions in both countries that possibly affected the presence of tourists on the beaches and conditioned the presence of anthropogenic pollutants. Interestingly, common UVFs, such as avobenzone were not found at concentrations above its LOD (0.01 μg/L for Avobenzone) in any of the studied samples. This is also the case for other UVFs that were considered for inclusion in the 4th WL, such as the industrial UVF Drometrizole (UV P).

UVFs were detected in 43 sampling sites out of the 46 investigated. Samples collected in Mar Menor had the greatest variety of compounds per sample while the rest contained at least one of them. Fig. 2 shows the cumulative concentration of UVFs in the sampling sites and seasons (complete data on UVFs load for each site is presented in SI Table 2). Table 3 summarizes the measured concentrations of the studied compounds found in this study. The highest measured concentration was for BP4 (0.633 μg/L), followed by BP3 (0.432 μg/L), OC (0.321 μg/L), BP1 (0.211 μg/L), and BP8 (0.187 μg/L). Of the five compounds, BP3 has the highest levels with an overall mean of 0.274 μg/L and a median of 0.252 μg/L. All measured concentrations are listed in SI Data 1. The highest cumulative concentration of UVFs was found in samples from the VillananitosBeach (1.08 μg/L) in Mar Menor, Paço D'Arcos Beach (0.96 μg/L) in Lisbon, and Paraíso Beach (0.88 μg/L) also in Mar Menor.

Globally, BP3 and OC have been among the most commonly detected UVFs for their widespread use worldwide. Both have previously been detected in seawater and marine and coastal biota (Agawin et al., 2022; Bell et al., 2017; Cunha et al., 2018; Fenni et al., 2022; Gago-Ferrero et al., 2013; He et al., 2019; Bell et al., 2017; Molins-Delgado et al., 2018; Langford et al., 2015; Li et al., 2017; Sang and Leung, 2016). BP3 has been especially studied in corals (Downs et al., 2022a). Previous studies on Spanish coasts reported their presence in the Canary archipelago (Rodríguez et al., 2015) and on densely populated beaches in the Balearic archipelago during high tourist season (only BP3) (Tovar-Sánchez et al., 2013). OC is very lipophilic, and poorly soluble in water, but it is widely used alone and also to give more stability to other UVFs in wide ranges of the UV spectrum. Some studies suggest that BP3 is one of the UVFs that is best degraded by WWTPs being one of the main compounds detected in untreated wastewater samples but lower than others in treated sludge (Fagervold et al., 2021; Liu et al., 2015). This suggests that environmental concentration levels of BP3 could be mainly due to direct releases into recreational waters. On the other hand, BP4 may have a lower removal efficiency in WWTPs since it is easily found in treated wastewater in higher concentrations than other UVFs. (Molins-Delgado et al., 2016a; Rodil et al., 2012; Tsui et al., 2014). Also, BP4 was the most commonly UVF found in this study, possibly because this substance is very soluble in water, polar (it is a sulfonic acid) and is used in many PCPs (not only sunscreens) as well as for industrial uses. Moreover, since BP3 was banned in Palau and Hawaii, brands are now using BP4 which may have caused an increase in concentrations and frequencies of detections of this compound. BP4 has been less studied in marine or coastal waters but a recent study carried out in the Balearic archipelago by Agawin et al. (2022) detected diverse UVFs in *Posidonia oceanica* revealing their bioaccumulation potential for >20 years. Among the UVFs studied, concentration of BP4 wasreached 29 ng/g dw. In this case, a connection was established between tourism and wastewater discharges. Both BP3 metabolites (BP8 and BP1) have also been detected and reported previously in marine ecosystems and biota (Downs et al., 2022a; Cunha et al., 2018; Molins-Delgado et al., 2018; Sang and Leung, 2016; Tsui et al., 2015).

Table 2
Summary of toxicity benchmark values selected for the test compounds. All concentrations are expressed in μg/L

Compound	Source of data	Endpoint	Species	Effect measure	AF	Benchmark value	Source
Benzophenone-1	PNEC – QSAR	ChV	Green algae	330	1000	0.33	(1)
Dioxybenzone	PNEC – Experimental	14-d LOEC - Bleaching	*S. caliendrum*	250	50	5	(2)
Octocrylene	PNEC – Experimental	21-d EC50 – Repro.	D. magna	2.66	10	0.266	(3)
Oxybenzone	SSD	HC05 LCL	NA	5.2	1	5.2	(4)
Sulisobenzone	PNEC – Experimental	14-d NOEC - Growth	*P. promelas*	1048	50	20.96	(3)

(1) ECOSAR V2.0 (US EPA, 2017)
(2) He et al 2019
(3) ECHA as reported in NASEM 2022
(4) NASEM 2022

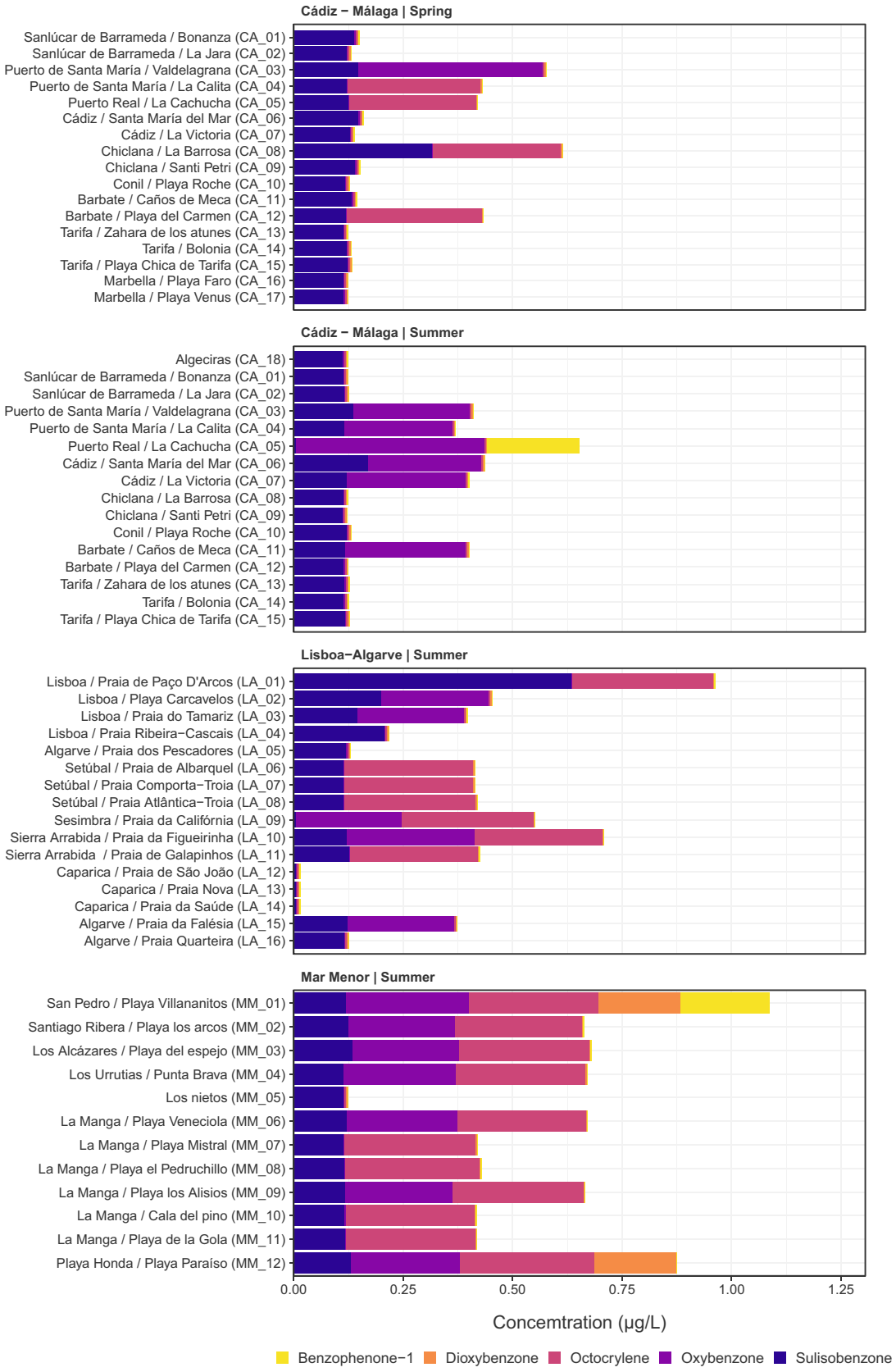

Fig. 2. Cumulative concentration of UV filters measured at the different sampling sites and seasons only compounds with at least one sample above LOD-were included.

Table 3
Detection frequency and summary statistics for the measured concentrations (for samples above the LOD) in the different areas and seasons (Data only for the 5 compounds detected at least one time above the LOD). Complete dataset with all measured data available on the supplemental information.

Compound	Area	Season	Detection freq. (%)	Median conc. (μg/L)	Mean conc. (μg/L)	Max conc. (μg/L)
Benzophenone-1	All areas	All seasons	3.3	0.208	0.208	0.211
	Cádiz - Málaga	Spring	0.00	-	-	-
	Cádiz - Málaga	Summer	6.3	0.211	0.211	0.211
	Lisboa - Algarve	Summer	0.00	-	-	-
	Mar Menor	Summer	8.3	0.206	0.206	0.206
Dioxybenzone	All areas	All seasons	3.3	0.187	0.187	0.187
	Cádiz - Málaga	Spring	0.00	-	-	-
	Cádiz - Málaga	Summer	0.00	-	-	-
	Lisboa - Algarve	Summer	0.00	-	-	-
	Mar Menor	Summer	16.7	0.187	0.187	0.187
Octocrylene	All areas	All seasons	36.07	0.295	0.298	0.321
	Cádiz - Málaga	Spring	23.5	0.297	0.298	0.308
	Cádiz - Málaga	Summer	0.00	-	-	-
	Lisboa - Algarve	Summer	43.8	0.294	0.298	0.321
	Mar Menor	Summer	91.7	0.296	0.297	0.307
Oxybenzone	All areas	All seasons	31.2	0.252	0.274	0.432
	Cádiz - Málaga	Spring	5.9	0.422	0.422	0.422
	Cádiz - Málaga	Summer	37.5	0.269	0.292	0.432
	Lisboa - Algarve	Summer	31.3	0.244	0.254	0.292
	Mar Menor	Summer	58.3	0.249	0.253	0.282
Sulisobenzone	All areas	All seasons	91.8	0.119	0.138	0.633
	Cádiz - Málaga	Spring	100	0.123	0.137	0.316
	Cádiz - Málaga	Summer	93.8	0.115	0.12	0.169
	Lisboa - Algarve	Summer	75	0.121	0.177	0.633
	Mar Menor	Summer	100	0.117	0.119	0.134

3.2. Ecological risk assessment

The results of our risk assessment show a low risk for BP1 at 2 points and a moderate risk for OC at 22 (Fig. 3). The measured concentrations for all other compounds are not expected to pose a risk when evaluating the compounds individually. Risk quotients for all samples are listed in SI Table 3. In this study, possible interactions of UVFs with other UVFs, metabolites, other substances and different environmental stressors, have not been considered in the risk assessment. Although some studies report possible synergistic or additive effects (NASEM, 2022), while others (Park et al., 2017; Molins-Delgado et al., 2016b) suggested an antagonistic effect of three UVFs, which produced a reduction of toxic effects in mixtures compared to individual effects. More data from reliable laboratory toxicity studies with multicomponent mixtures, different species in marine ecosystems and concentrations in marine sediments, due to the hydrophobicity of some UVFs, would be necessary to approach the real risk of these substances.

Our measured concentrations of BP1 were high enough to pose a low environmental risk to the aquatic environment in 2 out of the 61 samples collected (La Cachucha in Cádiz and Playa Villananitos in Mar Menor). Although we detected only two points with low risk, previous studies have founded a low-moderate risk for aquatic organisms at different trophic levels due to the reported estrogenic activity of this metabolite of BP3 (Tsui et al., 2015). While Downs et al. (2022a) reported that BP1 could be more toxic than the original compound, Molins-Delgado et al. (2016b) pointed out that this compound may increase its toxicity in combination with other substances. Although a low risk was reported at different trophic levels for BP1 (Tsui et al., 2014; Tsui et al., 2015), several authors have advised the importance of including metabolites in risk assessments, risk management, and regulations as they can increase the possible adverse effects (Mustieles et al., 2023; Ziarrusta et al., 2018). According to data published by NASEM (2022), BP8 has been observed to be more toxic than its parent compound and other metabolites, however, available literature together with the results of this study, indicate a low risk to ecosystems.

The risk detected for OC in this study is consistent with the results of previous studies that indicate a potential high environmental risk (Campos et al., 2017b; Pintado-Herrera et al., 2017; Schaap and Slijkerman, 2018). OC has been observed to affect the reproductive systems of fish and adversely affect their development (Yan et al., 2020). In fact, bioaccumulation and biomagnification data for this compound are higher than for other UVFs (Gago-Ferrero et al., 2013; Peng et al., 2017; Yang et al., 2020). Zhang et al. (2016) reported that the higher the level of accumulation, the more evidence of adverse effects. Despite this, some studies suggest that OC is not bioaccumulative according to the criteria established by ECHA and that there is no accumulation along the food chain (Pawlowski et al., 2019).

As highlighted in the NASEM report (NASEM, 2022) and also noted by several authors (Huang et al., 2021; Pintado-Herrera et al., 2017) a substantial limitation to the assessment of the environmental risk posed by UVFs, is the limited availability of reliable data, particularly experimental effects data from standardized test methods. As noted earlier, a sufficient number of reliable experimental data to allow for the development of an SSD was only available for BP3. The concentrations of this compound did not exceed the lower confidence level of the HC5 reported by NASEM (NASEM, 2022), which resulted in RQ values below 1, in fact, the highest measured BP3 concentration (0.43 μg/L, measured in Cádiz – Málaga in the summer), was approximately an order of magnitude lower than this HC5 LCL definer (5.2 μg/L). It is relevant to note that the HC5 LCL used as a benchmark in this study is higher than the PNEC listed for BP3 in the 4th Watchlist of the WFD (0.67 μg/L), however we believe the SSD-derived value provides a more realistic estimate of the hazard of the substance. In either case, the highest measured concentration of BP3 (0.43 μg/L) is still lower than the WL value, so the resulting RQs would have still been below 1 if that value had been used.

A small number of reliable laboratory toxicity studies were available for BP8, BP4, and OC (Table 2), however not in sufficient numbers to allow for the development of SSDs. Of these, only OC showed a moderate risk in our samples. As noted in the NASEM report, limited chronic toxicity data is available for this compound. The selected toxicity endpoint (2.66 μg/L) is a 21-d *Daphnia magna* EC50 for reproduction presented in the European Chemicals Agency (ECHA) dossiers and used as reported in NASEM (2022). This value is substantially lower than other reported chronic toxicity values. Additionally, an AF of 10 was applied to account for the limited amount of data available, so risk estimates for our samples may change as more data becomes available.

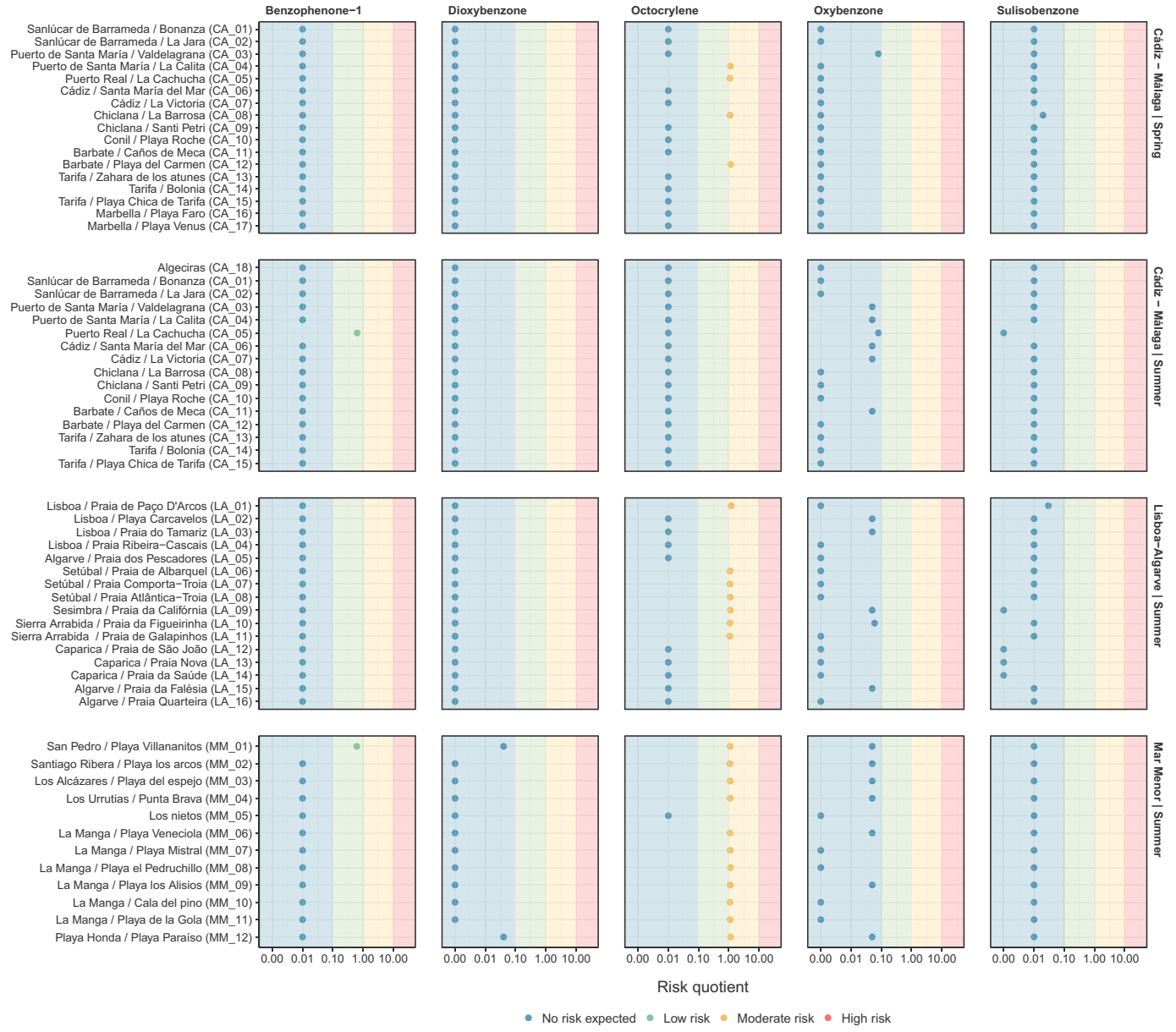

Fig. 3. Calculated Risk Quotients for the studied UV filters measured at the different sampling sites. Only data compounds for which at least one samples appeared above LOD. For those samples below it a value of ½ the LOD was used.

Nonetheless following our precautionary approach, OC does result in RQ values above one in ~1/3 of the collected samples. It is worth noting that the chosen PNEC for OC is the same as that proposed in the 4th WL (Gomez Cortes et al., 2022). As noted earlier, no experimental chronic toxicity data were available for BP1, so QSAR data was used instead. Due to the limited reliability of this approach, an AF of 1000 was required, likely influencing the measured risk.

Apart from the already mentioned factors (e.g., limited availability of ecotoxicity data) the risk estimates present several limitations as they consider only exposures from the water column and assess each chemical individually. Aspects such as bioaccumulation and biomagnification, effects of possible mixtures and geomorphological characteristics of the site that can condition photostability and possible biodegradation of UVFs could also play a substantial role in the risk UVFs may pose to coastal ecosystems. The involvement of non-standard endpoints for vulnerable or key species and also multi species in the risk assessment can affect the outcomes of these estimates (Campos et al., 2017a; Mitchelmore et al., 2021; NASEM, 2022).

Under laboratory conditions, BP8 and OC have shown low biodegradability while BP3 and BP4 are considered relatively biodegradable. However, this could vary in different environmental compartments (NASEM, 2022). Bioaccumulation does not occur equally for all species. Vidal-Liñán et al. (2018) suggest that current Kow-based bioconcentration models may underestimate the real risk. They also point out that possible biotransformations can occur in organisms. Limited data indicates BP3 and OC to be of low-moderate bioaccumulation potential, however, Vidal-Liñán et al. (2018) detected a remarkable accumulation of OC in mussels (along with BP4) while BP3 showed limited accumulation. Bioaccumulation for OC was also reported by Gago-Ferrero et al. (2013) in dolphin liver tissue and suggested a trophic transfer similar to Peng et al. (2017) who suggest the possible biomagnification for OC in marine food chains. In this study concentration in detritivorous fish was generally higher, although without significant differences. Gago-Ferrero et al. (2015) had already shown the bioaccumulation in freshwater food chain and indicated a possible trophic dilution for BP3. Even so, available information on the possible

biomagnification of most UVFs is still limited (Huang et al., 2021; NASEM, 2022).

Regulatory responses to the ubiquity and growing body of literature on the environmental effects of this class of compounds have become more pronounced in recent years. Some jurisdictions have even resorted to the use of restrictions. The Republic of Palau has the strictest regulation in the world prohibited since the adoption of these Regulations Prohibiting Reef-Toxic Sunscreen, a groundbreaking regulatory approach for sunscreens based on the precautionary principle that bans the manufacture, importation, and sale of sunscreens containing some chemical ingredients. The list of forbidden compounds currently includes BP3, BP4, BP8, and OC, all of them detected in this study, due to the evidence that certain UVFs contributed to coral bleaching. Other regions as Hawaii have already banned BP3 and this compound is also banned in Thailand, for the same reason. (Downs et al., 2022a; Mitchelmore et al., 2021; 2020 Tourism Authority of Thailand). Downs et al. (2022b) pointed out how proper tourism and sustainable management is essential to protect and preserve the most sensitive marine ecosystems and the way to advance in the recovery of those that have suffered consequences from UVFs pollution. Without this management, tourism on the coasts can be a threat to ecosystems. Policies adopted can also condition cosmetic industries to use environmentally safer formulations, as well as contribute to greater consumer awareness. In the meantime, alternative options for sunscreen could be made available for susceptible populations from health professionals and free online international databases with reliable ingredient information (Manová et al., 2015; Mustieles et al., 2023; NASEM, 2022).

3.3. Influencing factors

The RDA carried out in our study showed that the monitoring variables significantly explain the variance of the UVF exposure dataset (Monte Carlo *p*-value 0.006; Fig. 4). All variables for each point are in SI Table 4. The variables that contribute most to the variation are people influx, the sampling season, whether it was an open bay or not, and the level of urbanization. On the other hand, the proximity of WWTPs had a lower influence. The analysis showed a positive correlation between people influx, sampling during the summer season, and the level of urbanization with BP3, BP8 and BP1 concentrations, while OC and BP4 exposure increased in closed bays with less water exchange with the open sea.

In the Lisbon-Algarve area, the most detected substance was BP4 (75 % of the samples), compared to 44 % of the OC and 31 % of BP3. BP3's metabolites were not detected in any of the Portuguese samples. None of the 21 compounds analyzed were detected in either São João, Nova or da Saúde beaches. Moderate risk was detected on 7 beaches (Fig. 3). It is relevant that all of them were close to environmentally protected areas. Paço D'Arcos beach is especially noteworthy for being located at the river mouth of the Tagus River, close to Estuary Do Tejo estuary nature reserve. This beach contained the second overall highest total concentration of UVFs (0.96 ng/L), and it was the Portuguese location with the highest load of UVFs, and also contained the highest overall concentration of BP4 (0.63 μg/L), much higher than the rest of the samples collected in this study. The rest of the beaches, Albarquel, Comporta-Troia, Atlantica-Troia, California, Figuerinha and Galapinhos are located near the area of Estuary Do Sado. Praia da Figueirinha showed the second-highest cumulative load in this area (0.71 μg/L).

To gather some information on seasonality, the Cádiz–Málaga area

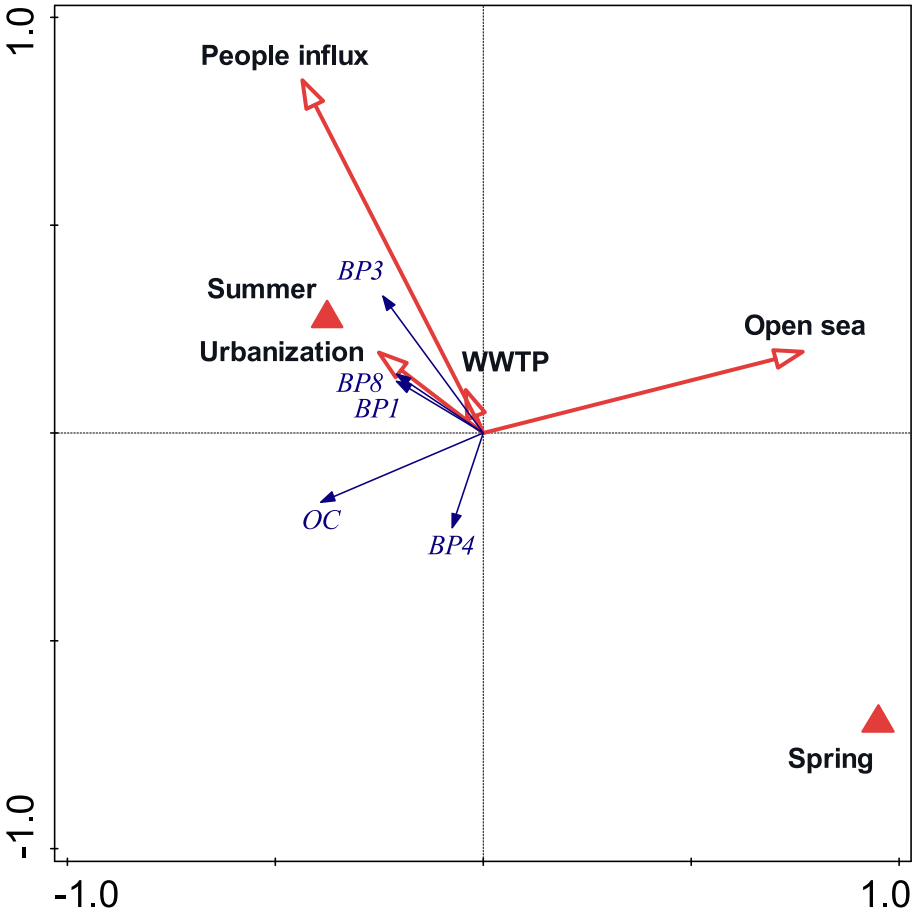

Fig. 4. Redundancy analysis of different influencing variables on UVF concentration.

was sampled both in the spring and summer. All samples from both spring and summer contained at least one of the studied UVFs. BP4 was the most commonly detected UVF appearing in 100 % of the spring samples and 93.8 % of the summer samples. BP8 was not detected in any of the seasons, while OC was not detected at all in the summer. Relatively high seasonal variability was observed between spring and summer. For example, the beach of La Barrosa (Chiclana) which had the highest load of UVFs, in the spring (0.61 μg/L), showed one of the lowest loads in the summer. Other beaches showed more consistency with similar concentrations in spring and summer. Valdegrana and La Calita in Puerto de Santa María and La Cachucha (Puerto Real) are good examples, with La Cachucha showing the highest UVF load in the summer (0.65 μg/L). Interestingly, the type of compounds detected in the spring tended to differ from those found in the summer, with OC being more common and abundant in the spring, while BP3 was more abundant in the summer. The samples containing the lowest load of UVFs were from Zahara de los Atunes (Tarifa) in the spring and Algeciras in the summer, both with 0.12 μg/L. In this area, low risk was detected only for an urban beach located in the bay of Cádiz (La Cachucha), for BP1 in summer sampling. In spring, moderate risk (OC) was detected for 4 beaches: La Calita, La Cachucha, La Barrosa and Nuestra Señora del Carmen beach. The four are urban beaches, located near the port of Cádiz, in the Bay of Cádiz, open sea (Atlantic Ocean) and the mouth of the Barbate river, respectively.

Samples from the Mar Menor area contained the greatest variety of compounds, and higher detection frequencies. As described, this area is a semi-closed saltwater lagoon badly affected by illegal dumping and its environmental degradation consequences. This area accomodates two sampling sites (San Pedro and Villananitos beaches) with the highest cumulative load of UVFs was measured in the whole study, the beaches of San Pedro or Villananitos, with 1.09 μg/L. The location with the lowest load in this area was Los Nietos Beach (0.11 μg/L). Once again, BP4 was the most commonly detected UVF appearing in 100 % of the samples, followed by BP3, in more than half of the samples (58 %) and OC in 11 of the 12 samples (92 %). In this case, BP1 and BP8 were also detected in one (8 %) and two samples (17 %), respectively. The sample with both metabolites was the most contaminated. Low risk (BP1) was detected only on Villananitos' beach, which was the most contaminated of all the points sampled. Moderate risk (OC) was also detected for this same beach. The rest of the beaches in this area also showed a moderate risk, except for Los Nietos, where no risk was detected.

4. Conclusions

UVFs are an integral part of our lives, both regarding their personal care, and industrial uses, however, it is important to balance the protection of human and environmental health. This study adds to the growing literature highlighting the ubiquity of UVFs in the environment, particularly in coastal waters. The link between the presence of these compounds in the environment with areas of high tourism and recreational use of seaside places is also shown. In relation to the specific objectives of this study, the identification and quantification of UVFs in waters of the Iberian Peninsula provide valuable information on the exposure data on coastal water bodies of the EU and therefore, may help on the goal of the 4th WL. In the same way, our study also supports the inclusion of BP3 and OC in the 4th WL by showing their ubiquity and the frequent risk posed by OC for marine ecosystems. The risk detected in some beaches close to protected natural areas deserves more attention. The concentration levels determined and the associated risks of UVFs are not worrisome, however, more specific studies should be carried out in these areas to determine the origin of these substances, as well as the toxicity of OC to marine organisms to refine risk assessments for coastal areas of high biodiversity such as those included in this study.

CRediT authorship contribution statement

Sandra Mozas-Blanco: Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **José Luis Rodríguez-Gil:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Judit Kalman:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Gerard Quintana:** Formal analysis, Investigation, Writing – original draft. **M. Silvia Díaz-Cruz:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Andreu Rico:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Isabel López-Heras:** Formal analysis, Writing – original draft. **Salomé Martínez-Morcillo:** Investigation, Writing – original draft, Writing – review & editing. **Miguel Motas:** Investigation, Writing – original draft. **Unax Lertxundi:** Investigation, Writing – original draft. **Gorka Orive:** Investigation, Writing – original draft. **Osvaldo Santos:** Investigation, Writing – original draft. **Yolanda Valcárcel:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft, 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.

Data availability

Data will be made available on request.

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References

Agawin, N.S.R., Sunyer-Caldú, A., Díaz-Cruz, M.S., Frank-Comas, A., García-Márquez, M. G., Tovar-Sánchez, A., 2022. Mediterranean seagrass Posidonia oceanica accumulates sunscreen UV filters. Mar. Pollut. Bull. 176, 113417. https://doi.org/10.1016/j.marpolbul.2022.113417.

Álvarez-Rogel, J., Barberá, G.G., Maxwell, B., Guerrero-Brotons, M., Díaz-García, C., Martínez-Sánchez, J.J., Sallent, A., Martínez-Ródenas, J., González-Alcaraz, M.N., Jiménez-Cárceles, F., Tercero, C., Gómez, R., 2020. The case of Mar Menor eutrophication: state of the art and description of tested nature-based solutions. Ecol. Eng. 158, 106086. https://doi.org/10.1016/j.ecoleng.2020.106086.

Apel, C., Tang, J., Ebinghaus, R., 2018. Environmental occurrence and distribution of organic UV stabilizers and UV filters in the sediment of Chinese Bohai and Yellow Seas. Environ. Pollut. 235, 85–94. https://doi.org/10.1016/j.envpol.2017.12.051.

Bell, L., Ucharm, G., Patris, S., Díaz-Cruz, M., Roig, M., Dawson, M., Coral Reef Research Foundation, 2017. Final report: Sunscreen pollution analysis in Jellyfish Lake. https://coralreefpalau.org/wp-content/uploads/2017/10/CRRF-UNESCOSunscreen-in-Jellyfish-Lake-no.2732.pdf.

Campos, D., Gravato, C., Fedorova, G., Burkina, V., Soares, A.M., Pestana, J.L., 2017a. Ecotoxicity of two organic UV-filters to the freshwater caddisfly Sericostoma vittatum. Environ. Pollut. 228, 370–377. https://doi.org/10.1016/j.envpol.2017.05.021.

Campos, D., Gravato, C., Quintaneiro, C., Golovko, O., Žlábek, V., Soares, A.M., Pestana, J.L., 2017b. Toxicity of organic UV-filters to the aquatic midge Chironomus riparius. Ecotoxicol. Environ. Saf. 143, 210–216. https://doi.org/10.1016/j.ecoenv.2017.05.005.

Connors, K.A., Beasley, A., Barron, M.G., Belanger, S.E., Bonnell, M.R., Brill, J.L., De Zwart, D., Kienzler, A., Krailler, J.M., Otter, R.R., Phillips, J.L., Embry, M.R., 2019.

Creation of a curated aquatic toxicology database: EnviroTox. Environ. Toxicol. Chem. 38 (5), 1062–1073. https://doi.org/10.1002/etc.4382.
Cunha, S.C., Trabalón, L., Jacobs, S., Castro, M., Fernández-Tejedor, M., Granby, K., Verbeke, W., Kwadijk, C., Ferrari, F., Robbens, J., Sioen, I., Pocurull, E., Marques, A., Fernandes, J.O., Domingo, J.L., 2018. UV-filters and musk fragrances in seafood commercialized in Europe Union: occurrence, risk and exposure assessment. Environ. Res. 161, 399–408. https://doi.org/10.1016/j.envres.2017.11.015.
Downs, C.A., Bishop, E., Díaz-Cruz, M.S., Haghshenas, S., Stien, D., Rodrigues, A.C., Woodley, C.M., Sunyer-Caldú, A., Doust, S.N., Espero, W., Ward, G., Farhangmehr, A., Samimi, S.M.T., Risk, M.J., Lebaron, P., DiNardo, J.C., 2022a. Oxybenzone contamination from sunscreen pollution and its ecological threat to Hanauma Bay, Oahu, Hawaii, U.S.A. Chemosphere 291, 132880. https://doi.org/10.1016/j.chemosphere.2021.132880.
Downs, C.A., Cruz, O., Remengesau, T.E., 2022b. Sunscreen pollution and tourism governance: science and innovation are necessary for biodiversity conservation and sustainable tourism. Aquatic Conservation-marine and Freshwater Ecosystems 32 (5), 896–906. https://doi.org/10.1002/aqc.3791.
Downs, C.A., Díaz-Cruz, M.S., White, W.B., Rice, M., Jim, L., Punihaole, C., Dant, M., Gautam, K., Woodley, C.M., Walsh, K.O., Perry, J., Downs, E.M., Bishop, L., Garg, A., King, K.A., Paltin, T., McKinley, E.B., Beers, A.I., Anbumani, S., Bagshaw, J., 2022c. Beach showers as sources of contamination for sunscreen pollution in marine protected areas and areas of intensive beach tourism in Hawaii, USA. J. Hazard. Mater. 438, 129546. https://doi.org/10.1016/j.jhazmat.2022.129546.
ECHA, 2011. Part B: Hazard assessment. In: Guidance on information requirements and chemical safety assess-ment. European Chemicals Agency, Helsinki. http://echa.europa.eu/documents/10162/13643/information_requirements_part_b_en.pdf.
ECHA, 2012. Part B: hazard assessment. In: Guidance on information requirements and chemical safety assessment. European Chemicals Agency, Helsinki. http://echa.europa.eu/documents/10162/13643/information_requirements_part_b_en.pdf.
Fagervold, S.K., Rohée, C., Rodrigues, A.B., Stien, D., Lebaron, P., 2021. Efficient degradation of the organic UV filter benzophenone-3 by Sphingomonas wittichii strain BP14P isolated from WWTP sludge. Sci. Total Environ. 758, 143674. https://doi.org/10.1016/j.scitotenv.2020.143674.
Fenni, F., Sunyer-Caldú, A., Mansour, H.B., Díaz-Cruz, M.S., 2022. Contaminants of emerging concern in marine areas: first evidence of UV filters and paraben preservatives in seawater and sediment on the eastern coast of Tunisia. Environ. Pollut. 309, 119749. https://doi.org/10.1016/j.envpol.2022.119749.
Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2012. An overview of UV-absorbing compounds (organic UV filters) in aquatic biota. Anal. Bioanal. Chem. 404 (9), 2597–2610. https://doi.org/10.1007/s00216-012-6067-7.
Gago-Ferrero, P., Alonso, M., Bertozzi, C.P., Marigo, J., Barbosa, L.A., Cremer, M.J., Secchi, E.R., Azevedo, A.F., Lailson-Brito, J., Torres, J.P., Malm, O., Eljarrat, E., Díaz-Cruz, M.S., Barceló, D., 2013. First determination of UV filters in marine mammals. Octocrylene levels in Franciscana dolphins. Environ. Sci. Technol. 47 (11), 5619–5625. https://doi.org/10.1021/es400675y.
Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2015. UV filters bioaccumulation in fish from Iberian River basins. Sci. Total Environ. 518-519, 518–525. https://doi.org/10.1016/j.scitotenv.2015.03.026.
Gasco Cavero, S., García-Gil, A., Cruz-Pérez, N., Rodríguez, L.F.M., Laspidou, C., Contreras-Llin, A., Quintana, G., Díaz-Cruz, S., Santamarta, J.C., 2023. First emerging pollutants profile in groundwater of the volcanic active island of El Hierro (Canary Islands). Sci. Total Environ. 872, 162204. https://doi.org/10.1016/j.scitotenv.2023.162204.
Gomez Cortes, L., Marinov, D., Sanseverino, I., Navarro Cuenca, A., Niegowska Conforti, M., Porcel Rodriguez, E., Stefanelli, F., Lettieri, T., 2022. Selection of substances for the 4th Watch List under the Water Framework Directive. Publications Office of the European Union, Luxembourg. https://doi.org/10.2760/01939. JRC130252.
He, K., Hain, E., Timm, A., Tarnowski, M., Wang, Y., 2019. Occurrence of antibiotics, estrogenic hormones, and UV-filters in water, sediment, and oyster tissue from the Chesapeake Bay. Sci. Total Environ. 650, 3101–3109. https://doi.org/10.1016/j.scitotenv.2018.10.021.
Huang, Y., Law, J.C., Lam, T., Leung, K.S., 2021. Risks of organic UV filters: a review of environmental and human health concern studies. Sci. Total Environ. 755, 142486. https://doi.org/10.1016/j.scitotenv.2020.142486.
Kim, K., Ekpeghere, K.I., Jeong, H.J., Oh, J., 2017. Effects of the summer holiday season on UV filter and illicit drug concentrations in the Korean wastewater system and aquatic environment. Environ. Pollut. 227, 587–595. https://doi.org/10.1016/j.envpol.2017.04.055.
Langford, K., Reid, M.J., Fjeld, E., Øxnevad, S., Thomas, K.V., 2015. Environmental occurrence and risk of organic UV filters and stabilizers in multiple matrices in Norway. Environ. Int. 80, 1–7. https://doi.org/10.1016/j.envint.2015.03.012.
Li, A.J., Sang, Z., Chow, C., Law, J.C., Guo, Y., Leung, K.S., 2017. Environmental behavior of 12 UV filters and photocatalytic profile of ethyl-4-aminobenzoate. J. Hazard. Mater. 337, 115–125. https://doi.org/10.1016/j.jhazmat.2017.04.067.
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.
Manová, E., Von Goetz, N., Hungerbuehler, K., 2015. Aggregate consumer exposure to UV filter ethylhexyl methoxycinnamate via personal care products. Environ. Int. 74, 249–257. https://doi.org/10.1016/j.envint.2014.09.008.
Mitchelmore, C.L., Burns, E.K., Conway, A., Heyes, A., Davies, I.A., 2021. A critical review of organic ultraviolet filter exposure, hazard, and risk to corals. Environ. Toxicol. Chem. 40 (4), 967–988. https://doi.org/10.1002/etc.4948.
Molins-Delgado, D., Díaz-Cruz, M.S., Barceló, D., 2016a. Ecological risk assessment associated to the removal of endocrine-disrupting parabens and benzophenone-4 in wastewater treatment. J. Hazard. Mater. 310, 143–151. https://doi.org/10.1016/j.jhazmat.2016.02.030.
Molins-Delgado, D., Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2016b. Single and joint ecotoxicity data estimation of organic UV filters and nanomaterials toward selected aquatic organisms. Urban groundwater risk assessment. Environ. Res. 145, 126–134. https://doi.org/10.1016/j.envres.2015.11.026.
Molins-Delgado, D., Muñoz, R., Nogueira, S., Alonso, M., Torres, J.P., Malm, O., Ziolli, 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.
Mustieles, V., Balogh, R.K., Axelstad, M., Montazeri, P., Márquez, S., Vrijheid, M., Draskau, M.K., Taxvig, C., Peinado, F.J.M., Berman, T., Frederiksen, H., Fernández, M.F., Vinggaard, A.M., Andersson, A., 2023. Benzophenone-3: comprehensive review of the toxicological and human evidence with meta-analysis of human biomonitoring studies. Environ. Int. 173, 107739. https://doi.org/10.1016/j.envint.2023.107739.
Paredes, E., Pérez, S., Rodil, R., Quintana, J.M., Beiras, R., 2014. Ecotoxicological evaluation of four UV filters using marine organisms from different trophic levels Isochrysis galbana, Mytilus galloprovincialis, Paracentrotus lividus, and Siriella armata. Chemosphere 104, 44–50. https://doi.org/10.1016/j.chemosphere.2013.10.053.
Park, C., Jang, J., Kim, S., 2017. Single- and mixture toxicity of three organic UV-filters, ethylhexyl methoxycinnamate, octocrylene, and avobenzone on Daphnia magna. Ecotoxicol. Environ. Saf. 137, 57–63. https://doi.org/10.1016/j.ecoenv.2016.11.017.
Pawlowski, S., Lanzinger, A.C., Dolich, T., Füßl, S., Salinas, E., Zok, S., Weiss, B., Hefner, N., Van Sloun, P.P.H., Hombeck, H., Klingelmann, E., Petersen-Thiery, M., 2019. Evaluation of the bioaccumulation of octocrylene after dietary and aqueous exposure. Sci. Total Environ. 672, 669–679. https://doi.org/10.1016/j.scitotenv.2019.03.237.
Peng, X., Fan, Y., Jin, J., Xiong, S., Liu, J., Tang, C., 2017. Bioaccumulation and biomagnification of ultraviolet absorbents in marine wildlife of the Pearl River Estuarine, South China Sea. Environ. Pollut. 225, 55–65. https://doi.org/10.1016/j.envpol.2017.03.035.
Pintado-Herrera, M.G., Combi, T., Corada-Fernández, C., González-Mazo, E., Lara-Martín, P.A., 2017. Occurrence and spatial distribution of legacy and emerging organic pollutants in marine sediments from the Atlantic coast (Andalusia, SW Spain). Sci. Total Environ. 605-606, 980–994. https://doi.org/10.1016/j.scitotenv.2017.06.055.
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.
Review of Fate, Exposure, and Effects of Sunscreens in Aquatic Environments and Implications for Sunscreen Usage and Human Health, 2022. National Academies of Sciences (NASEM). https://doi.org/10.17226/26381.
Rodil, R., Quintana, J.M., Concha-Graña, E., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2012. Emerging pollutants in sewage, surface and drinking water in Galicia (NW Spain). Chemosphere 86 (10), 1040–1049. https://doi.org/10.1016/j.chemosphere.2011.11.053.
Rodríguez, A., Sanz, M.R., Rodriguez, J.A., 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.
Ruiz-Fernández, J.M., León, V.M., Marín Guirao, L., Giménez Casalduero, F., Alvárez Rogel, J., Esteve Selma, M.A., Gómez, Cerezo R., Robledano, Aymerich F., González, Barberá G., Martínez Fernández, J., 2020. Synthesis report on the current state of the Mar Menor and its causes in relation to nutrient contents. In: Bulletin Administrative Litigation Commission. Environmental protection. Rights of Citizenship. No. 3.Volume II.
Sánchez-Ávila, J., Tauler, R., Lacorte, S., 2012. Organic micropollutants in coastal waters from NW Mediterranean Sea: sources distribution and potential risk. Environ. Int. 46, 50–62. https://doi.org/10.1016/j.envint.2012.04.013.
Sang, Z., Leung, K.S., 2016. Environmental occurrence and ecological risk assessment of organic UV filters in marine organisms from Hong Kong coastal waters. Sci. Total Environ. 566-567, 489–498. https://doi.org/10.1016/j.scitotenv.2016.05.120.
Schaap, I., Slijkerman, D., 2018. An environmental risk assessment of three organic UV-filters at Lac Bay, Bonaire, southern Caribbean. Mar. Pollut. Bull. 135, 490–495. https://doi.org/10.1016/j.marpolbul.2018.07.054.
Sharifan, H., 2020. Alarming the impacts of the organic and inorganic UV blockers on endangered coral's species in the Persian Gulf: a scientific concern for coral protection. Sustain. Futures 2, 100017. https://doi.org/10.1016/j.sftr.2020.100017.
Ter Braak, C.J.F., Šmilauer, P., 2012. Canoco Reference Manual and User's Guide: Software for Ordination (Version 5.0). Microcomputer Power, Ithaca, NY, USA, p. 496.
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 (6), e65451. https://doi.org/10.1371/journal.pone.0065451.
Tsui, M.M., Leung, H.Y., Lam, P.K., Murphy, M., 2014. 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.
Tsui, M.M., Leung, H.Y., Kwan, B.K.Y., Ng, K.M., Yamashita, N., Taniyasu, S., Lam, P.K., Murphy, M., 2015. Occurrence, distribution and ecological risk assessment of

multiple classes of UV filters in marine sediments in Hong Kong and Japan. J. Hazard. Mater. 292, 180–187. https://doi.org/10.1016/j.jhazmat.2015.03.025.
US EPA, 2017. Ecological Structure Activity Relationships (ECOSAR) Predictive Model. V2.0. U. S. Environmental Protection Agency, Washington DC.
US EPA, 2023. Ecotox User Guide: Ecotoxicology Knowledgebase System. Version 5.0. 2022. United States Environmental Protection Agency. Office of Pesticide Programs, Environmental Fate and Effects Division, United States EPA, Washington, D.C.
Vidal-Liñán, L., Villaverde-De-Sáa, E., Rodil, R., Quintana, J.M., Beiras, R., 2018. Bioaccumulation of UV filters in Mytilus galloprovincialis mussel. Chemosphere 190, 267–271. https://doi.org/10.1016/j.chemosphere.2017.09.144.
Yan, S., Liang, M., Chen, R., Hong, X., Zha, J., 2020. Reproductive toxicity and estrogen activity in Japanese medaka (Oryzias latipes) exposed to environmentally relevant concentrations of octocrylene. Environ. Pollut. 261, 114104. https://doi.org/10.1016/j.envpol.2020.114104.
Yang, H., Lu, G., Yan, Z., Liu, J., Dong, H., Bao, X., Xiadong, Z., Sun, Y., 2020. Residues, bioaccumulation, and trophic transfer of pharmaceuticals and personal care products in highly urbanized rivers affected by water diversion. J. Hazard. Mater. 391, 122245. https://doi.org/10.1016/j.jhazmat.2020.122245.
Zhang, Q., Y,X., MA, Wang, X.C., Ngo, H.H., 2016. Assessment of multiple hormone activities of a UV-filter (octocrylene) in zebrafish (Danio rerio). Chemosphere 159, 433–441. https://doi.org/10.1016/j.chemosphere.2016.06.037.
Ziarrusta, H., Mijangos, L., Montes, R., Rodil, R., Anakabe, E., Izagirre, U., Prieto, A., Etxebarria, N., Olivares, M., Zuloaga, O., 2018. Study of bioconcentration of oxybenzone in gilt-head bream and characterization of its by-products. Chemosphere 208, 399–407. https://doi.org/10.1016/j.chemosphere.2018.05.154.