Microchemical Journal 181 (2022) 107807

Contents lists available at ScienceDirect

Microchemical Journal

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

Occurrence and bioconcentration of organic UV filters in primary marine consumers

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ARTICLE INFO

Keywords:
Organic UV filters
Marine organisms
Microwave-assisted extraction
Bioconcentration
Biomagnification

ABSTRACT

Organic ultraviolet (UV) filters are added in different products to absorb UV radiation, whose use has been voiced due to increasing concerning about skin damage. Given their extensive production, these compounds are continuously released to the aquatic environment, which makes them an important family of emerging pollutants. Their presence in the marine environment poses a hazard to the living organisms exposed to them.

Primary marine consumers can be recognised as sentinels of pollution in marine environments. In this study, the occurrence of eight widely used organic UV filters was analysed in five different primary marine consumers from three beaches on the Gran Canaria Island (Spain) collected for 4 months. For that, a new method, based on microwave-assisted extraction and ultrahigh-performance liquid chromatography coupled to mass spectrometry in tandem, was optimized and validate. The developed method presented detection limits between 0.7 $ng \cdot g^{-1}$ dry weight (dw) and 7.1 $ng \cdot g^{-1}$ dw and intraday and interday precision with ranges from 0.2 % to 9.9 % and from 1.9 % to 12.4 %, respectively.

The method was applied to 20 samples comprising five different types of organisms. All the analysed samples revealed the presence of organic UV filters, in all samples at least one analyte was determined. The highest detection frequency corresponded to butyl methoxydibenzoylmethane (BMDBM) (55 %), while octocrylene (OC) was found at the highest concentration (1,735 $ng \cdot g^{-1}$ dw) in the sea hare *Aplysia dactylomela*.

At the same time, a preliminary bioconcentration and biomagnification assessment was made for the UV filters found in the studied marine organisms. Bioconcentration factors (Log values) over 3.7 were obtained in some cases, which suggests possible bioaccumulation. 4-methylbenzylidene camphor (4MBC) and drometrizole trisiloxane (DTS) obtained a biomagnification factor over 1, which implies potential biomagnification for these compounds.

1. Introduction

The use of organic ultraviolet (UV) filters has increased in the last century because of awareness of sun radiation effects on skin. These compounds are mainly added in personal care products (PCPs), but are also used for other purposes, such as food packaging, paints, textiles, industrial goods, etc. [1]. Given their extensive use, they are continuously released to terrestrial [2] and aquatic environments [2,3].

Organic UV filters enter marine aquatic media via two pathways; direct input, which takes place from being washed off from skin during recreational activities; indirect input, associated with the release of wastewater outfall and river discharge [2] (Fig. 1). Because of their uninterrupted input to the aquatic environment, they are considered an important group of emerging pollutants. Therefore, biota is continuously exposed to organic UV filters. The inputs to the marine environment are presented in Fig. 1. In fact several studies have already reported their presence in different organisms [3,4].

Research into hazardous effects on marine species have increased in the last decade [5,6]. Some studies suggest adverse effects on different marine organisms for short exposures to organic UV filters, such as coral bleaching, mortality, endocrine disruption or diminished reproduction [5,6]. Given these adverse effects, Hawaii, the Republic of Palau and the US Virgin Islands have banned the use of benzophenone-3 (BP3) and octocrylene (OC), while the European Union has lowered the BP3 concentration allowed in cosmetics [7]. Nevertheless, long-term effects could result in greater damage to the marine biota besides the

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https://doi.org/10.1016/j.microc.2022.107807
Received 22 June 2022; Received in revised form 11 July 2022; Accepted 18 July 2022
Available online 25 July 2022

biomagnification effect of xenobiotics [8]. Coastal species are especially subjected to the anthropogenic impact [9].

The study of the occurrence of organic UV filters has focused mostly on fish [2] due to the concern of them reaching humans beings [5]. However, small organisms may be more likely affected by the presence of these compounds [6]. Higher concentrations of organic UV filters have been reported in the marine biota than in the fresh biota. Hence it is important to determine their presence and possible associated negative impacts on marine species [8].

In aquatic organisms, the potential uptake mechanisms of contaminants can follow two pathways. The direct uptake consists in passive absorption from the environment to exposed surfaces of organisms (*i.e.* respiratory and dermal surfaces). The indirect uptake is related to diet [10]. Direct absorption involves bioconcentration and indirect absorption entails biomagnification processes [11]. Approaches to estimate these mechanisms are important for reducing the uncertainty about the hazards and risks that those compounds pose to organisms.

In this context, primary marine consumers can be recognised as sentinels of pollution in marine environments. Thus, the aims of this work were, on the one hand, to develop a new method based on microwave-assisted extraction and ultrahigh-performance liquid chromatography coupled to mass spectrometry in tandem for the determination of eight organic UV filters in different species of primary marine consumers, and on the other hand, make a preliminary assessment of their possible bioconcentration and biomagnification through the trophic chain.

This study included five different species of primary marine consumers (two sea snails, the detritivore sea cucumber, an algae feeder sea hare, and the filtering sponge), which were recovered on three beaches of the Gran Canaria Island (Canary Islands) with different tourism pressures and characteristics.

The Gran Canaria Island (Spain) was selected as an interesting study site because of the many visitors that arrive there all year long. Moreover, previous studies have determined the target compounds in seawater [12], sediment [13] and macrophytes [14] from the beaches included in this work. Some of these compounds were also found in fish from Canary Islands [15], however, for the best of our knowledge, primary consumers from this region have not been investigated regarding the presence of organic UV filters. Since there is no available information about the levels of organic UV filter contaminations in this type of organisms, this work represents an opportunity to estimate bioconcentration processes for first time.

Given the detection of organic UV filters in different matrices, it is important to determine them in primary marine organisms to identify possible accumulation through the food web. In this sense, the extraction method developed in this work can be used to determine the anthropogenic pollution of organic UV filters of a wide range of physicochemical characteristic, in primary marine consumers.

2. Materials and methods

2.1. Reagents

Eight organic UV filters, namely homosalate (HMS), 4-methylbenzylidene camphor (4MBC), benzophenone-3 (BP3), drometrizole trisiloxane (DTS), octocrylene (OC), butyl methoxydibenzoylmethane (BMDBM), isoamyl p-methoxicinnamate (IMC) and methylene bis-benzotriazolyltetramethylbutylphenol (MBP) of analytical grade (purity ≥ 99 %), were purchased from Sigma-Aldrich (Madrid, Spain). Panreac Química (Barcelona, Spain) supplied methanol (MeOH), acetone, hexane (Hex), water and formic acid of LC-MS grade.

The stock solution of the target compounds (250 $mg \cdot L^{-1}$) was prepared in acetone and stored in amber glass bottles in a freezer until used. Working solutions were prepared daily in MeOH.

2.2. Study area, sample collection and pretreatment

The samples of organisms to be analysed were collected from three beaches on the Gran Canaria Island (Canary Islands, Spain), namely Las Canteras, Arinaga and Playa del Inglés.

Las Canteras beach is located in the northeast part of the Gran Canaria Island (28°8′27.982″N, 15°26′8.237″W), and is characterised by the presence of a rocky-sandy substratum [16] and a natural barrier that runs in parallel to its coast. This leads to lower water renovation at low tide because of almost no wave action [17], which might affect the local fauna due to the long residence time of pollutants. This beach is used mainly by locals, but also by foreigners, almost all year long, although the most intense tourism activity takes place in summer.

The Arinaga beach lies in the southeast part of the Gran Canaria Island (28°8′27.982″N, 15°26′8.237″W). It is an open beach characterised by the intense influence of wind and swell because of Trade winds and the Canary Current effect [18], which implies easy water renewal. It is

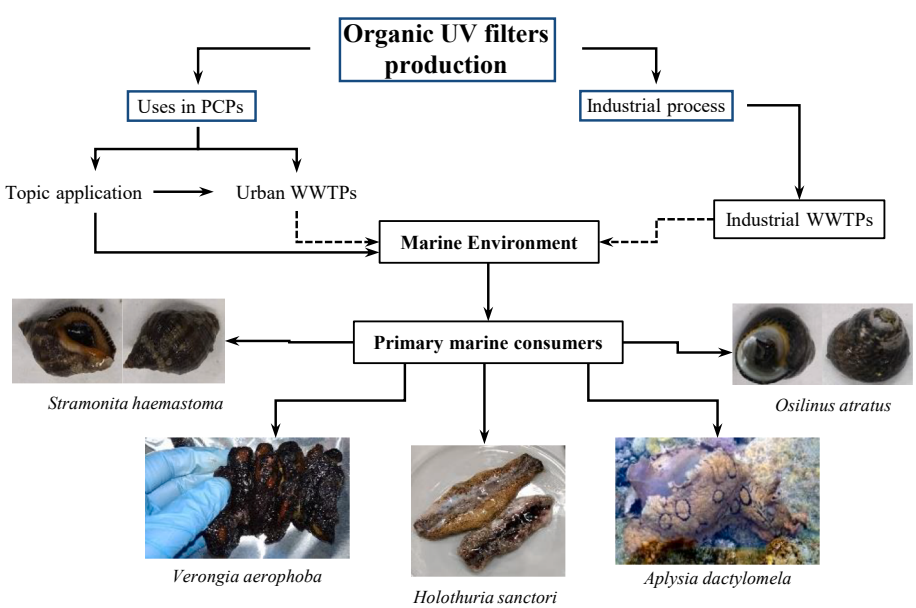

Fig. 1. Direct and indirect inputs to the marine environment. Indirect inputs are denoted by the dotted line.

used principally by locals, and scarcely by foreigners. This beach also presents a rocky-sandy substratum [16].

The Playa del Inglés beach is situated to the south of the Gran Canaria Island (27°45′23.579″N, 15°33′51.2809″W). This is an open beach with artificial barriers where the effect of Trade winds and the Canary Current is milder [18]. It is a quiet zone with a light swell that also presents a sandy substratum [16]. This beach is used all year round by international tourists, essentially northern Europeans in winter and national tourists in summer, according to the Gran Canaria Tourism Agency [19].

Primary marine consumers of five different species were taken monthly from October 2019 to January 2020. These organisms correspond to two sea snails, the herbivore *Phorcus atratus* (previously identified as *Osilinus atratus*) and the carnivorous *Stramonita haemastoma*, the detritivore sea cucumber (*Holothuria sanctori*), the algae feeder sea hare (*Aplysia dactylomela*), and the filtering sponge (*Aplysina aerophoba* that has been previously identified as *Verongia aerophoba*). This study examined 20 samples from the different organisms.

In order to compare the presence of organic UV filters between the different locations, sea snails (*Phorcus atratus*) of a similar size (1.8 – 2.9 cm length) were collected during the 4-month period at the three studied beaches in the rocky zone at low tide. On the Las Canteras beach, only *Phorcus atratus* was collected, while the two sea snail types (*Phorcus atratus* and *Stramonita haemastoma*) were collected on Playa del Inglés. On the Arinaga beach, four species were collected: *Phorcus atratus*, the sea cucumber, the sea hare, and the sponge. These organisms were collected at low tide, and only the organisms washed ashore were picked up. Therefore, different species were collected during each sampling.

After collection, samples were transported to the laboratory in glass bottles in a portable fridge. Upon arrival, they were rinsed with deionised water to remove sand and salt. The cleaned organisms were then identified, measured and frozen at –20 °C to be subjected to freeze-drying. The flesh of sea snails was separated from shells before the freeze-drying, while the whole body of the other organisms (sea cucumber, sea hare and sponge) was used. To obtain a homogenous sample, the freeze-dried tissues of each species were sifted through a < 300 μm particle size and stored in a fridge in the dark until analysed.

2.3. Preparing spiked samples and MAE extraction

The sea snail *Phorcus atratus* was employed for extraction optimisation purposes because this species was present on all the sampled beaches throughout the sampling period. The batch sample was spiked with a mixture of the target compounds, stirred, and air-dried at room temperature in the dark for 24 h to obtain a homogeneous dry sample.

One hundred milligrams of the spiked mixture were transferred to MAE vessels and 5 mL of acetone were added as an extractant. Then vessels were closed and sonicated for 2 min to homogenise the sample and extractant. The MAE process consisted in applying 50 °C for 3 min. Having completed extraction, the extract was carefully filtered through a 0.2 μm syringe filter. Then the filtered extract was transferred to LC vials and 10 μL was injected.

2.4. Instrumental analysis

Organic UV filters extraction was carried out in a Titan MPS microwave oven equipped with 16 TFM vessels (Perkin Elmer, Madrid, Spain).

Determination was performed by 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). The MassLynx Mass Spectrometry software (Waters Chromatography, Barcelona, Spain) controlled all the components.

Chromatographic conditions were previously optimised [12]. Briefly, the mobile phase consisted of MeOH (A) and water (B) LC-MS grade, each with 0.1 % (*v/v*) formic acid, at a flow rate of 0.3 $mL \cdot min^{-1}$. Detailed information about the mass conditions is reported in the Supplementary Material (Table S1).

2.5. Bioconcentration and biomagnification calculation

The bioconcentration factor (BCF) is calculated as the ratio between the pollutant concentration detected in the organisms and the pollutant concentration in the surrounding environment using the following formula [20]:

$$BCF = \frac{C_{organisms}}{C_{water}}$$

where $C_{organisms}$ is the concentration of the pollutant found in this study for the different target organisms (expressed as $mg \cdot kg^{-1}$ dry weight, dw) and C_{water} is the concentration (expressed as $mg \cdot L^{-1}$) measured in the seawater on the same beaches [12]. According to the European Commission, a substance is considered "very bioaccumulative" when the BCF is higher than 5,000 or Log BCF > 3.7 [20].

The bioaccumulation factor (BMF) is calculated as the ratio of the contaminant in the consumer to its concentration in food or prey by the following formula [21]:

$$BMF = \frac{C_{consumer}}{C_{food}}$$

where $C_{consumer}$ is the concentration (expressed as $ng \cdot g^{-1}$ dw) of the pollutant found in this study for the target marine organisms and C_{food} is the concentration in the consumer food (expressed as $ng \cdot g^{-1}$ dw) [22], taken from the data acquired for the same compounds in the seaweeds on the same beaches [14]. A BMF above 1 suggests the biomagnification of the contaminant from lower trophic chain levels [4,21].

3. Results and discussion

3.1. Microwave-assisted extraction

The impacts of temperature, extraction time, extractant volume and solvent type on the extraction efficiency of the target analytes were assessed with a 2^4 experimental design (four variables at two levels) built with the MiniTab software as a first approach. This consisted in 16 runs that combined temperatures at 50 °C and 60 °C; extraction time at 3 and 6 min; extractant volume at 2.5 and 5 mL; MeOH and acetone as extractants. With the obtained results, a Pareto Chart analysis was performed to see which variables affected extraction the most. They are denoted in blue in Fig. 2 for IMC. The variables showing the strongest effect were extractant volume and solvent type. Acetone performed better recoveries than MeOH for five compounds. The correlations between the variables were also analysed by Pearson's coefficient (0 means no influence; –1 is the maximum negative effect; 1 represents the maximum positive effect). The extractant volume obtained the highest values, with positive correlations between 0.1 and 0.7 for all the compounds, while temperature presented a negative correlation (except for BP3), which varied between –0.6 and –0.3. The lowest correlation was for the extraction time (from –0.3 to –0.1). The positive effect on the extractant volume means that the higher the volume, the more positive the influence on recoveries. The negative effect on both temperature and extraction time means that the higher the temperature and the longer the time, the more negative the influence on recoveries. For this reason, temperature was set at 50 °C and the extraction time was 3 min. Therefore, extractant type and volume were analysed in more depth.

In a second stage, a 3^2 factorial design (two variables at three levels) was applied with the aforementioned fixed variables. The two-target variables, namely extractant volume (5, 7.5 and 10 mL) and solvent type (acetone, hexane and MeOH), were studied. The best recoveries were obtained with 5 mL of acetone. As an example of the general observed trend, the surface response obtained for the DTS compound

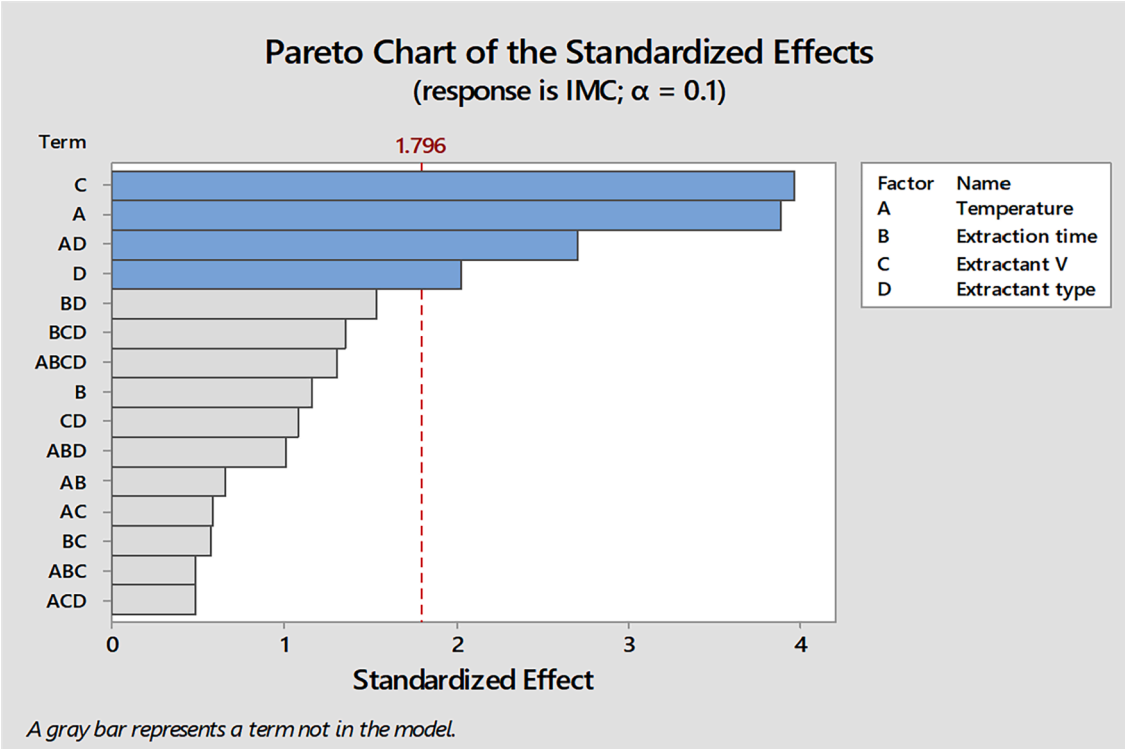

Fig. 2. Pareto chart of the standardised effects for the factors studied in the 2^4 experimental design on compound IMC.

from this design is shown in Fig. 3.

Therefore, the optimised conditions were: 5 mL of acetone as the extractant by applying 50 °C for 3 min.

3.2. Quality assurance and method validation

The linearity, method limits of detection (MLODs), method limits of quantification (MLOQs), precision and extraction efficiencies were evaluated under the optimum extraction conditions for the batch of sea

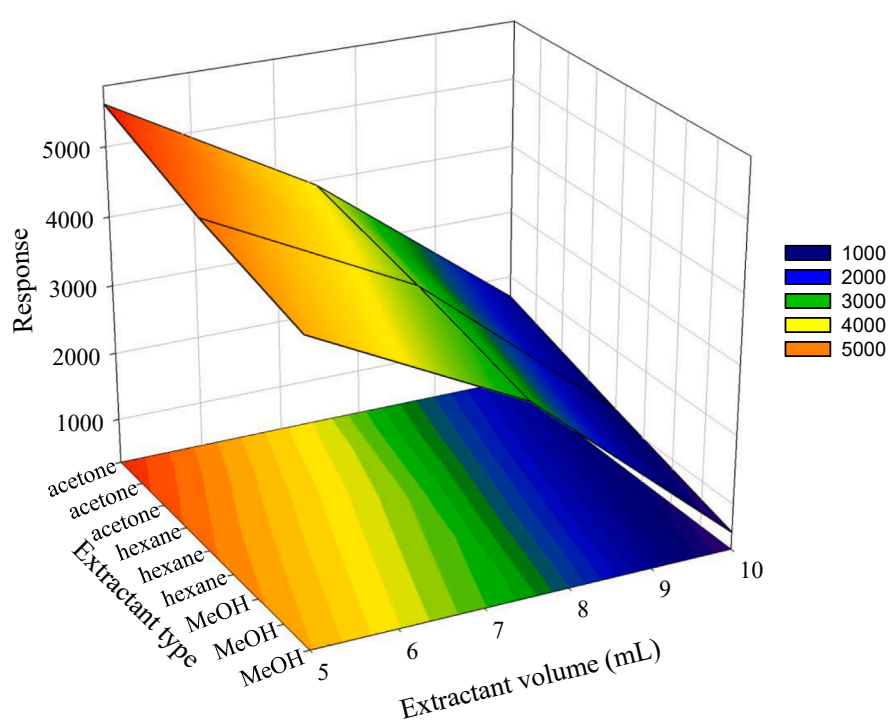

Fig. 3. Response surface for the effect of the extractant volume and type in compound DTS.

snails (*Phorcus atratus*). Each value corresponded to the mean of three replicates.

Calibration curves were built by means of the matrix matched calibration method at eight concentration levels of a mixture of the target compounds within the range from 7.5 ng·g^{-1} dw to 25,000 ng·g^{-1} dw. The linear correlation coefficient obtained for each compound within this range was > 0.99.

MLODs and MLOQs were calculated from the signal-to-noise (S/N) of each compound by assuming a minimum detectable limit of 3 and 10-fold the S/N, respectively. MLODs ranged between 0.7 ng·g^{-1} dw and 7.1 ng·g^{-1} dw, while MLOQs varied from 2.3 ng·g^{-1} dw to 23.8 ng·g^{-1} dw (Table 1).

The precision and extraction efficiencies were calculated at three concentrations levels (37.5, 250, 1,250 ng·g^{-1} dw) by comparing the signal from the standard solution to those obtained after applying the complete extraction method to the spiked samples.

The intraday (n = 3) and interday (k = 3) precisions of the developed method were estimated as relative standard deviation (RSD, %), which ranged from 0.2 % to 9.9 % and from 1.9 % to 12.4 %, respectively (Table 1).

Extraction efficiencies fell within the range from 31 % to 94 % (Table 1). The optimised method was validated for the other organisms. It gave similar recoveries and concentrations were adjusted to each obtained efficiency.

3.3. Environmental occurrence of organic UV filters in primary marine consumers

The developed analytical method was applied to determine the target analytes in five species of primary marine consumers and comprised 20 samples taken from three beaches of the Gran Canaria Island for 4 months. The measured concentrations and detection frequencies are summarised and presented in Table S2.

At least one compound was identified in each analysed marine organism (Fig. 4). Seven compounds presented detection frequencies between 10 % and 55 %, while BP3 was detected in only one sample. BMDBM (55 %) and OC (40 %) were the most frequently detected compounds, and fell within concentration ranges from 9.7 to 88.2 ng·g^{-1} dw and from 33.1 to 1,735 ng·g^{-1} dw, respectively. The highest detected concentrations corresponded to OC (1,735 ng·g^{-1} dw) in sea hare (*Aplysia dactylomela*) and to HMS (1,113 ng·g^{-1} dw) in sea cucumber (*Holothuria sanctori*).

The scarce detection frequency of BP3 in the marine organisms could be due to its lowest octanol–water coefficient (Log K_{ow}) value and the greatest water solubility among the target compounds (Table S1). This compound is considered readily biodegradable [23]. BP3 was found in a degraded state in the seawater enriched with dissolved organic matter [24] and some ligands [25]. Furthermore based on the Log K_{ow} approach, a passively partition according to their chemical affinity was assumed that did not take into account the metabolic biotransformation of organisms [26]. For example, BP3 can be degraded by microalgae into less toxic intermediates, which has been reported for *Scenedesmus obliquus* in freshwater [27]. However, BP3 has not been detected in a freshwater mussel (*Dreissena polymorpha*), which did accumulate other organic UV filters [28]. This falls in line with the scarce detection of BP3 in this study, which also agrees with its low bioaccumulation reported in the marine mussel *Mytilus galloprovincialis* [26].

The highest found concentration for OC can be explained by this compound being considered not easily biodegradable [23]. It had a high Log K_{ow} and low solubility (Table S1), which contribute to its bioaccumulation. This compound is extensively used in PCPs formulations [29] and is allowed in all countries [30,31]. The high OC concentration herein detected agrees with the found marine mussels *Mytilus galloprovincialis*, for which rapid uptake and a low depuration rate have been reported [26]. Nevertheless, the concentration of lipophilic compounds can be underestimated due to biotransformation products, as demonstrated for OC in marine corals [32] and a marine sediment worm species [33] for being transformed into fatty acid conjugates. Hence the actual accumulation of some compounds in the food web could be greater.

According to the concentrations found per location, on the Las Canteras beach BMDBM was the only target compound detected in all the samples (Table S2), which also presented the highest concentration (61.8 ng·g^{-1} dw). OC was present in 50 % of the samples and also at a high concentration (43.7 ng·g^{-1} dw) for *Phorcus atratus*. On the Arinaga Beach, almost all the compounds were reported, except MBP. OC (1,735 ng·g^{-1} dw) and HMS (1,113 ng·g^{-1} dw) had the highest concentrations for *Aplysia dactylomela* and *Holothuria sanctori*, respectively. Finally on the Playa Inglés beach, BMDBM was present in 50 % of the samples. On this beach HMS was measured at the highest concentration (1,003 ng·g^{-1} dw) for *Stramonita haemastoma*.

Taking into account the concentrations found in *Phorcus atratus* on all the beaches, Playa del Inglés was the location most contaminated by the target compounds, where the cumulative concentration of all the pollutants was 1,085 ng·g^{-1} dw, followed by the Las Canteras beach (260 ng·g^{-1} dw) and the Arinaga beach (248 ng·g^{-1} dw).

After considering the presence of the target analytes in all studied primary marine consumers, Playa del Inglés obtained the most contaminants (Fig. 4). In addition, the maximum concentrations appeared in the largest organisms (*i.e.* sea hare and sea cucumber), and also in the carnivorous sea snail (*Stramonita haemastoma*). These variations in the measured concentrations might be related to the potential species-specific differences in the uptake, accumulation, metabolism [4,34] and depuration rates [26] of the different marine organisms.

The results obtained in this work for primary marine consumers were compared to those found in previous studies for seawater [12] and

Table 1
Analytical parameters for the MAE-UHPLC-MS/MS method (concentrations expressed in dw).

Compounds	Intra-day precision (%)[a]			Inter-day precision (%)[b]			Recoveries (%)[c]			MLODs[d]	MLOQs[e]
	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	37.5 ng·g^{-1}	250 ng·g^{-1}	1250 ng·g^{-1}	ng·g^{-1}	ng·g^{-1}
4MBC	–	6.7	5.2	–	12.4	8.1	–	89	94	7.1	23.8
BP3	9.5	2.0	5.1	10.2	6.9	6.3	41	52	63	1.1	3.7
HMS	5.6	4.8	3.9	10.6	8.2	6.8	43	52	80	1.8	6.0
DTS	9.9	8.1	0.9	11.7	9.5	9.1	31	41	51	1.3	4.4
OC	9.3	5.7	1.0	9.8	5.2	1.9	65	68	93	1.9	6.3
BMDBM	3.6	3.1	0.2	5.2	6.0	4.8	84	88	91	1.4	4.6
IMC	5.2	4.8	1.9	11.5	8.5	8.7	59	62	73	0.7	2.3
MBP	–	6.1	4.9	–	10.4	9.5	–	64	82	7.0	23.3

[a] Mean of three replicates (n = 3).
[b] Mean of three replicates performed for three days (k = 3).
[c] Extraction efficiencies using *Phorcus atratus*.
[d] Calculated from the signal to noise (S/N) assuming a minimum detectable limit of three times the S/N.
[e] Calculated from the S/N assuming a minimum detectable limit of ten times the S/N.

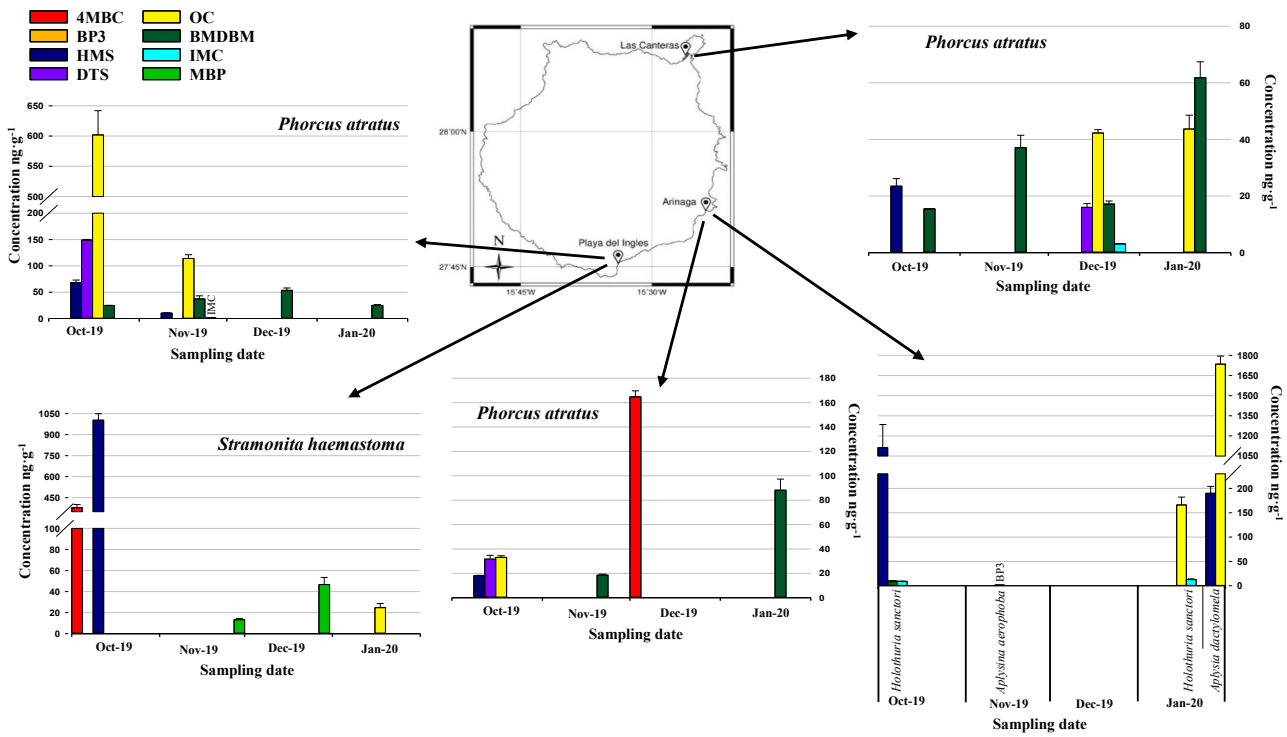

Fig. 4. Occurrence of organic UV filters in primary marine consumers from selected locations.

macrophytes samples [14] from the same beaches. In three studies, OC had the highest concentrations (172 μg·L^{-1} in seawater, 19,369 ng·g^{-1} dw in macrophytes and 1,735 ng·g^{-1} dw in primary marine consumers). According to the overall detection frequency in the three matrices, a tendency was observed: BMDBM, HMS and OC were the most commonly found compounds in primary marine consumers and macrophytes, while they were detected in<56 % of the samples in seawater. This can be explained by their high Log K_{ow} (>4.5) and poor solubility (<0.04) that, therefore, allow these compounds to be more easily distributed in solid matrices. The comparison of the concentrations found in this study to those reported in seawater demonstrated accumulation in solid matrices.

Otherwise in compounds BP3 and IMC, a contrary trend in their frequencies appeared because they were detected in over 78 % of the seawater samples, but this percentage was below 25 % in the organism samples. Such behaviour can be explained because these compounds presented the highest solubility and the lowest Log K_{ow} (Table S1) of the target compounds.

The detection of the target compounds in macrophytes and marine animals and their concentration levels indicated that these organisms could be used as bioindicators of organic UV filters contamination in coastal areas.

3.4. Global comparison

Organic UV filters have been registered in aquatic systems since the early 1980 s, but mainly in freshwater environments [35]. However, high concentrations are presently reported in marine ecosystems as a consequence of recreational activities and wastewater release to these media [3]. As all the target compounds were detected at least once in the different analysed primary marine consumers (Table S2), these concentrations will be discussed in relation to other wild primary marine organisms.

In this study, OC was detected at concentrations up to 1,735 ng·g^{-1} dw in sea hare. This level is comparable to those found for mussel on the French Mediterranean coast [36] and in coral in Hawaii [37], where samples were collected in areas impacted by human activities. This compound has been analysed in several mussel species, mainly from European countries by measuring concentrations generally within the 1.4 – 3,992 ng·g^{-1} dw range [8,29,35,38–42]. However in the study of Bachelot et al. [35], OC is reported in mussels from the French coast at a higher concentration (7,112 ng·g^{-1} dw) in August. Furthermore, OC has been reported in other organisms like clams, conchs, shrimps, sea urchin, oysters [8,29,38,43], corals [34], crabs [44] and squids [21] from Spain, China, Norway, and the USA.

The values of the HMS concentrations found in this study were also high (1,113 ng·g^{-1} dw), which is higher than those reported for oysters (56.1 – 211 ng·g^{-1} dw) [38,43] collected in the USA. This compound has also been detected in mussels and corals from different European countries, Hawaii and the USA within the range from 24.2 to 611.2 ng·g^{-1} dw [37,38,42].

The same case occurred for 4MBC. The concentrations reported in this study (165 – 379 ng·g^{-1} dw) are higher than those indicated for sea snails (whelk), mussels, clams, conchs, shrimps, sea urchins, octopus and crabs (0.2 – 102 ng·g^{-1} dw) from China and other European countries [8,40,42,45,46]. 4MBC has also been reported in squids, prawns, shrimps and crabs [21] from China within the 2 – 38.9 ng·g^{-1} lw range.

BMDBM was detected within the concentration 9.7 – 88.2 ng·g^{-1} dw range, which is lower than those reported for corals in Hawaii (4.8 – 291.3 ng·g^{-1} dw) [37]. This compound has also been found in stone crabs at 21 ng·g^{-1} lw from China [21].

Compound IMC was detected at concentrations from 1.5 to 12.8 ng·g^{-1} dw. Higher concentrations have been observed for mussels from Portugal (43.1 ng·g^{-1} dw) [46] and of other European origins (37.3 ng·g^{-1} dw) [42].

BP3 was detected only once in sponge (*Aplysina aerophoba*) in this study, but it could not be not quantified. It has also gone undetected in mussels from Spanish and Italian coasts [29]. Nevertheless, this compound has been quantified in several marine organisms [3] from

different places around the world, even in Antarctic clams (at 112 ng·g^{-1} dw) [47]. In mollusc bivalves (mussels, oysters, clams, conchs), levels of 0.9 – 622.1 ng·g^{-1} dw have been reported from China [8], the USA [38,43] and some European countries [40,42,46]. In echinoderms (sea cucumber and sea urchin), it has been recorded in the Antarctic [47], China [8] and Spain [48]. BP3 has been reported in arthropods (shrimps and Squilla) [8,42,45] and in cephalopods (squids) [45] from Europe and China. This compound has also been reported in corals from Hawaii [37], and in shrimps, crabs and corals [34,44] from Norway and China. The study of Peng et al. [21] has reported BP3 in squids, prawns, shrimps and crabs from China.

Finally, MBP was found in two samples in this study, at 13.3 and 46.7 ng·g^{-1} dw, and has not been reported in other primary marine consumers, only in fish [13,49].

In summary, organic UV filters have been reported in many primary marine consumers worldwide, and seem to accumulate by following similar patterns to polychlorinated biphenyls [50], which persist in the environment [51] and potentially reach upper trophic levels, such as marine mammals [52] and marine birds [28]. Rodil et al. [40] reported greater abundance for some organic UV filters than polycyclic aromatic hydrocarbons in mussels from Spain.

Transformation products, metabolites, photodegradation products and disinfection by-products should be determined because the biological process may be stereoselective (preferential accumulation for one structural form over others) [4], as suggested for 4MBC in lake fish [53]. Therefore, to reliably estimate organic UV filter bioavailability, bioaccumulation and biomagnification through the food web, these products should be taken into account [4].

A recent study has reported BP3 biodegradation products in seawater, sediment and two green seaweeds, and some have been detected in 100 % samples [54]. Nevertheless, depuration rates, metabolism, and excretion of organic UV filters for marine organisms are scarcely reported. The study by Cleargeaud et al. [33] suggests that the determination of only parent organic UV filters may underestimate the real exposure of organisms to xenobiotics and their metabolites. Further studies should be conducted in this field because some organic UV filters show similar toxicity to trace metals, such as copper, mercury, cadmium and zinc, and can reach different marine organisms [55].

3.5. Preliminary bioconcentration and biomagnification assessment

The presence of organic UV filters in previous studies in seaweed and seawater suggests that marine organisms may be exposed to these pollutants through diet and from the environment. A preliminary assessment of their possible bioconcentration and biomagnification in different organisms was performed with the concentrations that we obtained and those found before in seaweed [14] and seawater [12] on the same beaches. To do so, BCF was calculated using the minimum and maximum values of the target compounds in not only seawater, but also in each organism. For the BMF, the employed minimum and the maximum values were based on the possible seaweed species subjected to be eaten by *Phorcus atratus* [56] and *Aplysia dactylomela* [57–59]. The Log BCF and BMF results are summarised in Table 2.

The Log BCFs of all the found organic UV filters were above 3.7 (Table 2), which suggests bioaccumulation in the analysed primary marine consumers. The maximum BCF value was calculated for BMDBM on the Arinaga beach (Log BCF 8.6) for *Phorcus atratus*. The OC values are comparable to those reported in Hawaii for coral (Log BCF 3.4 – 6.1) [37], but higher than those reported in China (Log BCF 2.2 – 3.0) for coral [34] and mussels [26].

Lack of BP3 in marine organisms is explained because it can be eliminated by organisms, as Vidal-Liñá et al. [26] reported a quick elimination from mussels. Peng et al. [21] stated that this compound was not bioaccumulative because the concentration in carnivorous fish was lower than in detritivores ones. Nevertheless, BP3 accumulation has been reported in sea cucumber (*Holothuria tubulosa*) [48].

Regarding the BMF, only 4MBC and DTS obtained values above 1 for *Phorcus atratus*, which indicates possible biomagnification. The high BMF reported for 4MBC falls in line with the findings of benzophenone-4 in mussels, whose bioaccumulation was much greater than that predicted from its Log K_{ow} [26]. In addition, OC and HMS presented the lowest BMF (<0.3). Peng et al. [21] reported a BMF above 1 for OC in some marine organisms from the Pearl River (China). This difference could be attributed to the tendency of OC to form OC-fatty acids conjugated in some organisms, as previously mentioned.

The fate of organic UV filters at high trophic levels has been barely reported [9]. A study by Alonso et al. [60] found a higher concentration of organic UV filters and insecticides in a dolphin foetus than in the mother. Organic UV filters were found at higher concentrations than insecticides. These results suggest biomagnification at high trophic levels in the marine food web.

4. Conclusions

An analytical MAE-UHPLC-MS/MS method was successfully developed, validate, and applied to determine eight organic UV filters in five different primary marine consumers.

The highest concentration level was for OC (1,735 ng·g^{-1} dw) in sea hare (*Aplysia dactylomela*) in the Arinaga beach. This concentration corresponds to the largest studied organism, which can be attributed to

Table 2
Bioaccumulation for the target organic UV filters.

Bioconcentration factor (Log BCF)									
Sample location	**Organisms**	**Compounds**							
		4-MBC	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**IMC**	**MBP**
Las Canteras beach	*Phorcus atratus*	–*	–	5.8	7.6–5.8	6.9–5.4	8.2–5.8	5.9	–
Arinaga beach	*Phorcus atratus*	7.7	–	–	7.9–7.6	–	8.6	–	–
	Holothuria sanctori	–	–	–	–	–	7.7	7.9–7.4	–
Playa del Inglés beach	*Phorcus atratus*	–	–	7.4	–	8.4	6.9	5.9	–
	Stramonita haemastoma	–	–	8.6	–	7.0	–	–	–
Biomagnification factor (BMF)									
Sample location	**Organisms**	**Compounds**							
		4-MBC	**BP-3**	**HMS**	**DTS**	**OC**	**BMDBM**	**IMC**	**MBP**
Las Canteras beach	*Phorcus atratus*	–	–	0.01	1.1–0.1	0.05–0.01	0.3–0.1	0.9	–
Arinaga beach	*Phorcus atratus*	1.8	–	0.02	0.05	0.01	0.5	–	–
	Aplysia dactylomela	–	–	0.2	–	0.3	–	–	–
Playa del Inglés beach	*Phorcus atratus*	–	–	0.1	0.4	0.1	0.3	0.3	–

* The hyphen indicates that it was not possible to calculate the BCF and BMF.

its greater feeding behaviour *versus* the other analysed organisms. BMDBM showed the highest detection frequency of the target compounds. In contrast, BP3 was detected only once. The differences in the detection frequencies between these compounds can be attributed to their hydrophobicity behaviour, besides their different uses in PCPs, because BP3 presented a higher affinity for the aqueous phase than BMDBM.

According to the comparison made of the different marine matrices (seawater, macrophytes, primary marine consumers) in the same locations, OC obtained the highest concentration of all the target compounds. The frequency of detection of this compound was at its lowest in the aqueous phase (17 %), and its detection in the solid phases increased to>40 %. This fate can be explained by its high Log K_{ow} (6.88), which indicates a high affinity for solids. These results seem to indicate a pollution concern for OC in different marine compartments.

A preliminary bioconcentration (through BCF) and biomagnification (by means of the BMF) assessment was performed using previous data about the target compounds in seawater and seaweed, respectively. The reported Log BCF was over 3.7 for the quantified target compounds, which suggests their bioaccumulation in the studied marine organisms. Furthermore, the BMF found for 4MBC and DTS indicated possible biomagnification through the food web. Hence, the presence of organic UV filters in the analysed primary marine consumers can be attributed to the net absorption of compounds via all routes, which entails exposure from the surroundings and intake by the presence of pollutants in food.

Comprehensive research into the occurrence, bioaccumulation and biomagnification of these compounds is imperative to support adequate environmental management.

Due to the ecological relevance, further studies should be carried out in upper trophic organisms to a better understanding of the biomagnification of the target compounds. In addition, the possible metabolites should be considered to a real exposure evaluation.

CRediT authorship contribution statement

M. Isabel Cadena-Aizaga: Investigation, Methodology, Validation, Visualization, Writing – original draft. **Sarah Montesdeoca-Esponda:** Conceptualization, Supervision, Validation, Writing – review & editing. **Zoraida Sosa-Ferrera:** Conceptualization, Supervision, Validation, Resources. **José Juan Santana-Rodríguez:** Conceptualization, Writing – review & editing, Resources, Project administration.

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

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

Acknowledgments

M. Isabel Cadena-Aizaga would like to thank to University of Las Palmas de Gran Canaria (Spain) for her Ph.D. student grant.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2022.107807.

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