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Occurrence of eight UV filters in beaches of Gran Canaria (Canary Islands). An approach to environmental risk assessment



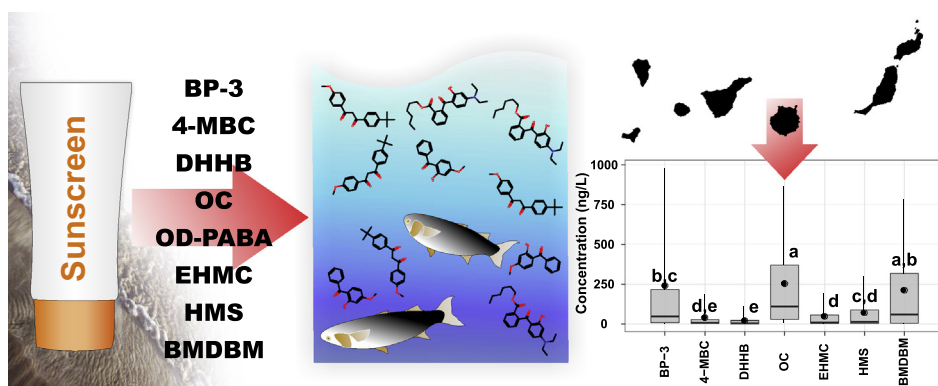
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HIGHLIGHTS

- UV filters levels in beach waters of Gran Canaria Island have been monitored.
- Highest levels were obtained for BP-3, BMDBM and OC UV filters.
- First time that DHHB levels are reported in coastal waters.
- Higher UV-filters levels were found in “semi-enclosed” beaches compared to open beaches.
- A preliminary risk assessment approach was applied for BP-3, 4-MBC and EHMC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 October 2014
 Received in revised form 6 February 2015
 Accepted 21 February 2015

Handling Editor: Caroline Gaus

Keywords:

UV filters
 Beaches
 Coastal water
 Environmental risk assessment

ABSTRACT

Due to the growing concern about human health effects of ultraviolet (UV) radiation, the use of UV filters has increased in recent decades. Unfortunately, some common UV filters are bioaccumulated in aquatic organisms and show a potential for estrogenic activity. The aim of the present study is to determine the presence of some UV filters in the coastal waters of six beaches around Gran Canaria Island as consequence of recreational seaside activities. Eight commonly used UV filters: benzophenone-3 (BP-3), octocrylene (OC), octyl-dimethyl-PABA (OD-PABA), ethylhexyl methoxy cinnamate (EHMC), homosalate (HMS), butyl methoxydibenzoyl methane (BMDBM), 4-methylbenzylidene camphor (4-MBC) and diethylamino hydroxybenzoyl hexyl benzoate (DHHB), were monitored and, with the exception of OD-PABA, all were detected in the samples collected. 99% of the samples showed some UV filters and concentration levels reached up to 3316.7 ng/L for BP-3. Environmental risk assessment (ERA) approach showed risk quotients (RQ) higher than 10, which means that there is a significant potential for adverse effects, for 4-MBC and EHMC for those samples with highest levels of UV filters.

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1. Introduction

UV filters are compounds employed in sunscreen and cosmetic formulations to protect the human skin from ultraviolet (UV) radiation. In order to protect the skin from the entire spectral

range, organic UVA and UVB filters are used together in products. UVA filters absorb radiation from 320 to 400 nm and UVB from 290 to 320 nm. Unfortunately, some of these compounds have undesirable effects on the skin such as sensitization, photoallergy or phototoxicity (Goossens et al., 1999; Giokas et al., 2007). Because of this, the European Community has established a list of UV filters allowed in cosmetic products and their maximum concentrations in ready-for-use preparations outlined in Annex VI of

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the Regulation on Cosmetic Products 1223/2009 (European Parliament, 2009). Some UV filters such as octocrylene (OC) and ethylhexyl methoxy cinnamate (EHMC) can be also used as UV light stabilizers in polymer-based products and some paints (Kameda et al., 2011). These compounds enter the aquatic media by wastewater treatment plants (WWTP) effluents (indirect input) or from skin washing during swimming, bathing or recreational activities (direct inputs). The presence of UV filters has been previously reported in coastal waters, river and lake waters, swimming pool waters, wastewaters (Poiger et al., 2004; Balmer et al., 2005; Giokas et al., 2004, 2005; Cuderman and Heath, 2007), as well as in sediments (Jeon et al., 2006) and in biota (Balmer et al., 2005; Buser et al., 2006).

UV filters in seawater can be found dissolved in the liquid phase or adsorbed on particulate matter. High concentrations of common UV filters like benzophenone-3 (BP-3) or 4-methylbenzylidene camphor (4-MBC) have been measured in the unfiltered fraction of the surface microlayer. Because of their lipophilic characteristics, these compounds tend to be more concentrated in the surface microlayer and accumulated in soils and particles (Tovar-Sánchez et al., 2013).

Methodologies for the determination of UV filters in environmental samples have been previously reviewed (Salvador and Chisvert, 2005; Peck, 2006; Giokas et al., 2007). Common analytical methodologies for determination in water samples include an extraction-preconcentration first step by means of solid phase extraction (SPE) (Langford and Thomas, 2008; Bratkovics and Sapozhnikova, 2011), in order to achieve low method limits of detection (MLOD). It is followed by gas chromatography (GC) (Cuderman and Heath, 2007) or liquid chromatography (LC) analysis (Rodil et al., 2012) coupled to mass spectrometry detectors. Not all UV filters are amenable for GC, so LC is the most suitable technique for their determination. On the other hand, in relatively clean water matrices, such as bathing-waters, expensive and sophisticated mass spectrometry detectors are not necessary and more common detectors, such as UV-photodiode array (PDA), are adequate for the determination of sunscreen agents (Giokas et al., 2005).

The growing concern about the environmental implications of UV filters has increased the number of studies in recent years. Due to their high lipophilicity ($\log K_{ow} = 3-7$) and stability in the environment, UV filters have been identified to have bioaccumulation factors greater than 5000 in fish (Brausch and Rand, 2011). Some of the UV filters such as 4-MBC and 3-benzylidene camphor have shown decreased reproduction and increased mortality rates of benthic organisms (Schmitt et al., 2008). In addition, some studies have indicated a significant potential for estrogenic activity (Schlumpf et al., 2001). In fact, benzophenone-1, BP-3, 4-MBC and EHMC have a similar estrogenic potential as well-known environmental estrogens like bisphenol A, methoxychlor, endosulfan or dibutylphthalate (Heneweer et al., 2005). Numerous UV filters can, potentially, cause coral bleaching (Danovaro et al., 2008) and estrogenic effects, and they may even adversely affect fecundity and reproduction in fish (Kunz et al., 2006; Coronado et al., 2008; Fent et al., 2008).

The Canary Islands is a Spanish archipelago located close to the northwest African coast, with tourism being the main economic activity of the region. It is the only European region where the bathing season is extended throughout all the year due to its mild weather. Moreover, Gran Canaria is one of most visited and populated island of the archipelago. Urban and resort areas are located close to the coast which are exposed to high human pressures. For this reason, the presence of new environmental pollutants is a priority that should be identified and controlled.

The aim of the present study was to determine the presence of eight common UV filters in the dissolved fraction of coastal waters from six beaches around Gran Canaria during 2011. Finally, an

Environmental Risk Assessment (ERA) approach was used to evaluate the potential impact of quantified UV filters levels. To the best of our knowledge, this is the first study which reports measurable levels of some common UV filters in the waters surrounding the Canary Islands.

2. Materials and methods

2.1. Monitored beaches and sampling

Six beaches located in Gran Canaria Island were selected for this study. Four of them (Maspalomas, MP; Puerto Rico, PR; Amadores, AM and Mogán, MG) are located in the southwest of the island, where most touristic activity is focused, and the remaining two (Las Alcaravaneras, AL and Las Canteras, CA) in Las Palmas de Gran Canaria (northeast), the main city of the archipelago. MP beach together with Playa del Inglés (the biggest resort area of Canary Islands), constitute a 6 km beach line. PR, AM and MG are small artificial sand beaches (250 m, 180 m and 800 m long respectively) characterized by the presence of artificial barriers. All of them are close to numerous resort complexes. These three beaches are designated as “semi-enclosed” in figures and discussion, while the others are denominated as “open”. On the other hand, AL and CA beaches are mostly visited by local residents. AL is a 550 m long beach surrounded by the island’s commercial harbour, whereas CA is a 4 km long beach which is the main leisure area of the city.

2.2. Reagents and chemicals

BP-3, OC, octyl-dimethyl-PABA (OD-PABA), EHMC, homosalate (HMS) and butyl methoxydibenzoyl methane (BMDBM) were purchased from Merck (Germany). 4-MBC and diethylamino hydroxybenzoyl hexyl benzoate (DHBB) were supplied by Dr. Ehrenstorfer (Germany). Stock standard solutions were prepared in methanol at 100 mg/L and stored in dark at 4 °C.

Methanol (HPLC gradient and residue analysis grades), acetone (HPLC grade), dichloromethane and ethyl acetate (residue analysis grades) were supplied by Scharlab (Spain). Hydrochloric acid (HCl 37%, v/v) was provided by Panreac (Spain) and orthophosphoric acid (H₃PO₄ 85%, v/v) by Merck (Germany). Ultra-high-quality water (Milli-Q water) was obtained from a Milli-Q purification system (Millipore, USA).

Glass fiber filters (47 mm and 0.7 µm pore size) and hydrophilic PTFE syringe filters (4 mm and 0.2 µm pore size) were supplied by Millipore (USA). Strata X SPE cartridges (500 mg, 6 mL) were provided by Phenomenex (Spain).

2.3. Analytical procedure

2.3.1. Sampling

Beach water samples were collected twice a month from May to October and monthly for the rest of 2011. One sample was collected at each beach on each sampling date and a total of 108 samples were collected. For all the beaches a sampling point location was established, at sites where a high affluence of bathers was observed. Samples were taken between 10 a.m. and 5 p.m. 1 L amber glass bottles were used; these were washed with marine water at the sample point and filled up at 1–1.5 m depth. Samples were stored in the dark at 4 °C until extraction within 24 h of the collection.

2.3.2. UV filters extraction and determination

Once the samples (1 L) arrived at the laboratory, 50 mL of methanol was added and pH was adjusted to 3. Then, samples were filtered with 0.7 µm glass fiber filters in order to avoid the clogging of SPE cartridges. The SPE procedure is based on a previous study (Cuderman and Heath, 2007) with modifications.

Briefly, a Strata X cartridge (500 mg and 6 mL) was subsequently conditioned with 3×3 mL ethyl acetate/dichloromethane (1/1, v/v), 3×3 mL methanol and 3×3 mL Milli-Q water, then the sample was passed through solid phase at a flow-rate of 8 mL/min. Then, the cartridge was washed with 3×3 mL of methanol (15%, v/v) and dried under a N_2 stream. Retained analytes were eluted with 3×3 mL ethyl acetate/dichloromethane (1/1, v/v) and the extract was evaporated to dryness under a gentle stream of N_2 . Finally, extracts were reconstituted to 0.2 mL of the mobile phase employed in UPLC-DAD determination. This procedure results in a preconcentration factor of 5000.

Analyte determination was performed in a Waters ACQUITY UPLC system consisting of a binary pump coupled to an autosampler and a photodiode array detector (PDA eλ ACQUITY UPLC). The stationary phase was a Waters ACQUITY BEH Shield RP18 (2.1×150 mm, $1.7 \mu\text{m}$ particle size) column set at 45°C . The chromatographic separation was carried out under isocratic conditions with 77% (v/v) of methanol and 23% (v/v) of H_3PO_4 (0.5%, v/v) at a flow rate of 0.42 mL/min. A volume of $5 \mu\text{L}$ of sample extract was injected into the system. The identification of analytes was conducted making use of retention times and absorbance spectra comparison with a standards library created with this purpose. Detailed analytical procedures and quantification and validation parameters are shown in [Supplementary Data](#).

2.4. Statistical analysis

In order to determine spatial and temporal distributions, statistical analyses were performed using the statistical package R ([R Development Core Team, 2013](#)). Censored data were transformed into half of respective MLOD or method limit of quantification (MLOQ) and included in the data set previous to statistical treatment in order to minimize type I error ([Clarke, 1998](#)). Non-parametric tests, Kruskal–Wallis and Wilcoxon–Mann–Whitney with Bonferroni correction, were performed with a 0.05 significance level.

3. Results and discussions

3.1. UV filters levels

All UV filters in study, excepting OD-PABA, were detected in the collected beach water samples. In 99% of the 108 samples collected and analyzed, at least one or more UV filters were quantified.

Distribution of quantified concentrations of UV filters found in all samples and the significant differences obtained between

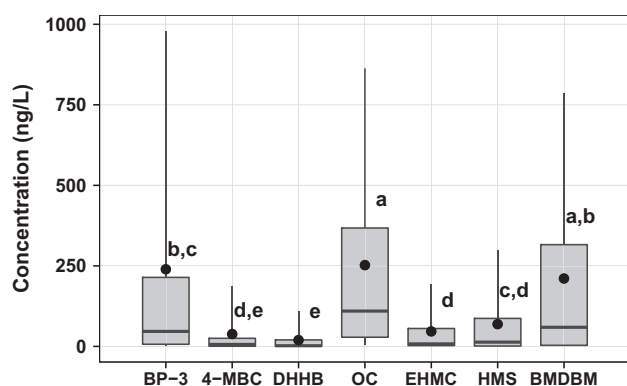


Fig. 1. Distribution levels of UV filters determined (letters show statistical differences: a is significantly higher than b, b higher than c, c higher than d, and d higher than e). Significance level = 0.05. Lower and upper whiskers represent 5th and 95th percentiles, lower and upper box limits represent 25th and 75th percentiles, horizontal lines inside boxes represent the median (50th percentile) and dots the average of each group of data.

compounds are shown in [Fig. 1](#). OC, BMDMB and BP-3 showed the highest levels and frequencies, with median values of 109.7 ng/L, 59.4 ng/L and 46.6 ng/L respectively. These three compounds represent an average of 80% of $\sum\text{UV}$ filter concentration. HMS presented lower concentrations (median = 13.3 ng/L), although no significant differences could be established for BP-3. The lowest concentrations were obtained for EHMC (median = 7.9 ng/L), 4-MBC (median = 6.3 ng/L) and DHHB (median = 2.1 ng/L).

The highest concentrations of $\sum\text{UV}$ filters were determined for those beaches with a “semi-enclosed” profile, PR (median = 1344.4 ng/L), MG (median = 1576.7 ng/L) and AM (median = 330.9 ng/L) and the lowest for those with an “open” profile, CA (median = 94.3 ng/L), AL (median = 33.3 ng/L) and MP (median = 37.4 ng/L) ([Fig. 2](#)). AM seems to present lower UV filter levels than MG and PR, but no significant differences could be determined as with AM and CA. On the other hand, CA showed higher concentrations than MP and AL, but again, no significant differences could be established. Temporal evaluation of $\sum\text{UV}$ filter levels at each beach is shown in [Fig. 3](#). Beaches located in the southwest of the island (MG, PR and AM) showed an increase of $\sum\text{UV}$ filter levels from May to November, with exception of MP. Whereas CA and AL, located in Las Palmas de Gran Canaria city, reached highest concentrations from August to mid-October.

Median, 95th percentile, concentration range and detection frequencies of UV filters in beach water samples are shown in [Table 1](#). Individual analysis of UV filters revealed higher levels for MG, PR and AM beaches, and this result is consistent with the $\sum\text{UV}$ filters observed in [Fig. 2](#). In fact, maximum concentration of BP-3 (3316.7 ng/L), OC (1324.9 ng/L) and BMDMB (1770.3 ng/L) were determined in MG, whereas maximum for EHMC (756.4 ng/L), HMS (536.2 ng/L) and DHHB (228.7 ng/L) were measured in PR. The highest concentration of 4-MBC (1043.4 ng/L) was quantified in CA. Additionally, all beaches seem to share a similar UV filter profile, the highest levels were obtained for OC, BMDMB and BP-3, followed by HMS and EHMC and the lowest levels were for 4-MBC and DHHB.

To the best of our knowledge, only one study has been carried out in a similar context in (“semi-enclosed” and densely populated beaches from resort areas of Majorca) Spain ([Tovar-Sánchez et al., 2013](#)). In this study, organic UV filters BP-3 and 4-MBC were analyzed during the high season (August–September 2011) and the maximum levels of both compounds found were about one order of magnitude lower than those reported in the present study.

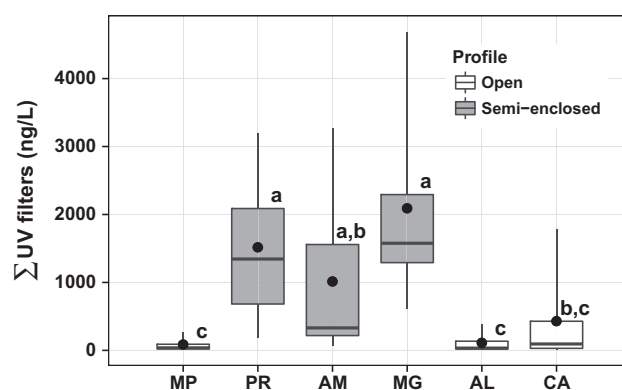


Fig. 2. Distribution levels of $\sum\text{UV}$ filters determined in each beach (letters show statistical differences: a is significantly higher than b and c, and b higher than c). Significance level = 0.05. Lower and upper whiskers represent the 5th and 95th percentiles, lower and upper box limits represent 25th and 75th percentiles, horizontal lines inside boxes represent the median (50th percentile) and dots the average of each group of data.

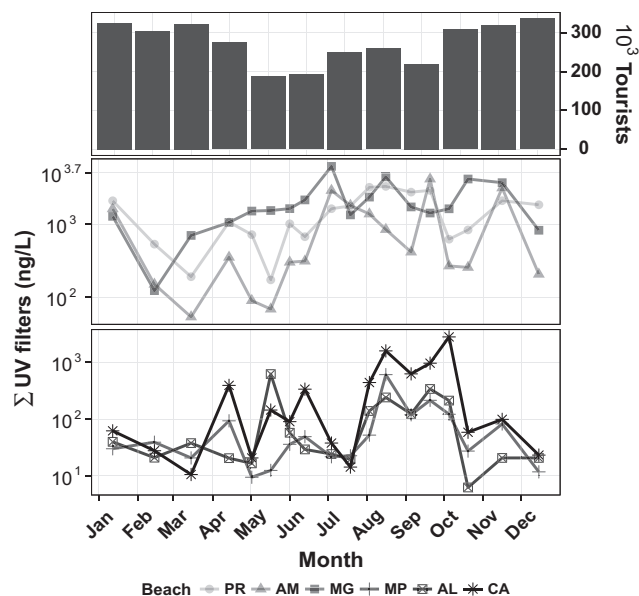


Fig. 3. Evolution of Σ UV filters concentrations during sampling period (January–December, 2011) in each beach. Upper plot shows tourists arrivals during 2011 (ISTAC, 2011).

OD-PABA was not detected in any sample. This was expected as OD-PABA is a derivate compound of p-aminobenzoic acid (PABA), which presents a photoallergic potential for humans (Waters et al., 2009). For this reason, PABA and its by-products have been progressively excluded from sunscreens formulations, although OD-PABA is still included as UV filter in the 1223/2009 European Regulation on cosmetic products (European Parliament, 2009).

BP-3 high levels found in beach waters could be explained on the basis of its higher water solubility, since this UV filter exhibits the lowest $\log K_{ow}$ (3.79) of all UV filters under study (Díaz-Cruz et al., 2008). However, despite the lower solubility of OC and BMDBM ($\log K_{ow}$ of 6.1 and 6.9 respectively; Kaiser et al., 2012) and high affinity for particulate matter, the high values of these compounds found could be a consequence of their extensive use in sunscreen formulations. BMDBM is the most widely used commercially available UVA filter (Shaath, 2005). This compound exhibits a high absorbance capacity in UVA range, but unfortunately it suffers a pronounced decomposition under sunlight radiation. For this reason, BMDBM is usually employed with OC to prevent its quick degradation. In fact, OC presents a moderate extinction coefficient and it is fundamentally used as BMDBM photostabilizer (Scalia and Mezzena, 2009). This joint use and similar $\log K_{ow}$ values are consistent with the strongest correlation found between concentration levels of compound pair (Pearson correlation coefficient ≈ 0.88).

DHHB also known as “Univul A Plus” was the last organic UV filter approved for use in cosmetics under 2005/9/EC Directive (European Commission, 2005) and, it is considered the principal alternative to BMDBM. As far as we know, this is the first study which reports DHHB measurable concentrations in coastal waters, although it was only determined at levels above its MLOD in 60% of samples. Its relatively recent insertion in the cosmetic market could be a reason for this lower frequency, but more attention should be paid to DHHB on account of the relatively limited scientific data available regarding its human and environmental impact.

The differences obtained among beaches could be attributed to their profile, size and affluence of bathers. PR, AM and MG are artificial crowded beaches protected by physical barriers which restrict water exchange and hence Σ UV filters concentrations increase. On the other hand, MP and CA beaches are also highly visited, but their “open” profiles and extensions (>1 km) favor a

Table 1
Statistical descriptors about UV filters occurrence and concentrations for monitored beaches.

Beach	Parameter	Compound						
		BP-3	4-MBC	DHHB	OC	EHMC	HMS	BMDBM
MP	Frequency (%) ^a	56%	33%	11%	100%	39%	22%	72%
	Range (ng/L)	<1.4 ^b –27.1	<0.9 ^b –7.2	<1.3 ^b < 4.2 ^c	<9.3 ^c –359.1	<1.6 ^b –16.1	<2.4 ^b –51.5	<2.0 ^b –188.4
	Median (ng/L)	4.6	<0.9 ^b	<1.3 ^b	23.8	<1.6 ^b	<2.4 ^b	<6.7 ^c
	P ₉₅ (ng/L) ^d	23.5	7.0	<1.3 ^b	177.4	14.7	49.7	144.3
PR	Frequency (%) ^a	100%	100%	100%	100%	94%	100%	100%
	Range (ng/L)	32.7–979.8	4.1–219.5	<4.2 ^c –228.7	61.2–973.1	<1.6 ^b –756.4	9.2–536.2	35.6–1163.2
	Median (ng/L)	238.7	26.8	14.7	374.5	71.0	60.6	307.5
	P ₉₅ (ng/L) ^d	979.5	214.5	160.3	891.0	508.1	333.1	819.7
AM	Frequency (%) ^a	100%	89%	83%	100%	94%	89%	100%
	Range (ng/L)	12.7–2675.7	<0.9 ^b –104.8	<1.3 ^b –163.5	30.7–766.7	<1.6 ^b –276.8	<2.4 ^b –319.0	<6.7 ^c –792.0
	Median (ng/L)	91.0	7.9	4.85	160.4	10.5	24.3	65.5
	P ₉₅ (ng/L) ^d	1593.6	55.7	119.5	667.2	206.0	254.0	558.6
MG	Frequency (%) ^a	100%	100%	100%	100%	100%	100%	100%
	Range (ng/L)	54.2–3316.7	<3.1 ^c –346.3	<4.2 ^c –144.4	37.8–1324.9	<5.2 ^c –260.2	10.8–526.1	19.8–1770.3
	Median (ng/L)	343.2	46.1	29.6	497.8	57.2	151.7	422.6
	P ₉₅ (ng/L) ^d	1567.7	312.6	100.3	1263.2	202.8	473.9	1223.4
AL	Frequency (%) ^a	61%	44%	22%	94%	61%	28%	67%
	Range (ng/L)	<1.4 ^b –158.0	<0.9 ^b –29.7	<1.3 ^b –34.7	<2.8 ^b –183.2	<1.6 ^b –65.4	<2.4 ^b –84.8	<2.0 ^b –314.3
	Median (ng/L)	3.7	<0.9 ^b	<1.3 ^b	20.9	<5.2 ^c	<2.4 ^b	<6.7 ^c
	P ₉₅ (ng/L) ^d	108.4	26.3	33.3	160.2	53.2	26.7	259.4
CA	Frequency (%) ^a	72%	56%	44%	94%	72%	39%	83%
	Range (ng/L)	<1.4 ^b –182.6	<0.9 ^b –1043.4	<1.3 ^b –176.3	<2.8 ^b –768.5	<1.6 ^b –109.9	<2.4 ^b –102.2	<2.0 ^b –737.1
	Median (ng/L)	9.6	2.3	<1.3 ^b	52.7	7.3	<2.4 ^b	23.5
	P ₉₅ (ng/L) ^d	165.4	668.6	147.8	620.5	94.5	86.3	640.9

^a Frequency of samples which presents a concentration above its LOD.

^b LOD.

^c LOQ.

^d P₉₅: 95th percentile concentration.

higher water exchange which benefit lower \sum UV filter concentrations.

In similar studies, sampling dates were established during summer time, (Poiger et al., 2004; Balmer et al., 2005; Giokas et al., 2005; Langford and Thomas, 2008). However, in the Canary Islands the bathing season lasts nearly all year and, consequently, the temporal fluctuation of UV filters concentrations during winter and summer is less pronounced. The differences of \sum UV filters temporal evolution (Fig. 3) can be attributed to users' habits. Foreign bathers prevail during all year (ISTAC, 2011) on the beaches of the southwest of the island (PR, AM, MG, MP), while city beaches (AL and CA) are principally frequented by local users with more pronounced seasonal habits.

3.2. Environmental risk assessment approach

The risk assessment was conducted only for BP-3, 4-MBC and EHMC using chronic toxicity data available in scientific literature. Risk quotients (RQ) for these three substances, were calculated as a ratio between its measured environmental concentrations obtained in this study (MEC) and the predicted no effect concentrations (PNEC), calculated dividing the no-observed effect concentrations (NOECs) by a safety factor. Risk classification was based on the criteria adopted by several authors (Marcus et al., 2010; Sánchez-Avila et al., 2012), in which if $RQ < 1$ no significant risk can be expected, if $1 \leq RQ < 10$ there is a small potential for adverse effects, $10 \leq RQ < 100$ there is a significant potential for adverse effects and if $RQ \geq 100$, adverse effects should be expected.

In this work, RQ was calculated for the worst case scenario using the maximum MEC (RQ_{max}) as well as the 95th percentile MEC value (RQ_{95}) for each compound in every sampled beach in order to be more conservative, as well as to obtain more representative results (Von der Ohe et al., 2011). In both cases, NOECs for the crustacean *Daphnia magna* (Sieratowicz et al., 2011) were used with an safety factor of 1000 as it is stated in the Technical Guidance Document for the marine aquatic compartment (European Chemicals Bureau, 2003). Table 2 summarizes the results of these calculations.

Significant potential for adverse effects were found for 4-MBC in CA beach and particularly for EHMC at PR beach, where both values of RQ_{max} and RQ_{95} were >10 . Small potential for adverse effects were found for BP-3 at three (PR, AM and MG) of the monitored beaches, for 4-MBC at three of them (PR, AM, MG) and for EHMC at four beaches (AM, MG, AL and CA). Only at MP beach no significant risk was found for any of these substances.

These results represent merely a first approach. One cannot rule out a possible environmental risk based on limited toxicity data of some UV filters compounds on particular freshwater specie. More research on the environmental effects and toxicities of all common UV filters for aquatic marine organisms should be carried out in order to determine more accurately the overall risk associated with UV-filters. As stated in other studies (Fent et al., 2010), acute toxicity in *D. magna* increases with the lipophilicity of compounds.

Table 2
Risk assessment approach for BP-3, 4-MBC and EHMC in waters of monitored beaches.

Compound	NOEC (mg/L)	PNEC (ng/L)	RQ ₅	Beach					
				MP	PR	AM	MG	AL	CA
BP-3	0.5	500	RQ _{max}	0.1	2.0	5.4	6.6	0.3	0.4
			RQ ₉₅	0.0	2.0	3.2	3.1	0.2	0.3
4-MBC	0.1	100	RQ _{max}	0.1	2.2	1.0	3.5	0.3	10.4
			RQ ₉₅	0.1	2.1	0.6	3.1	0.3	6.7
EHMC	0.04	40	RQ _{max}	0.4	18.9	6.9	6.5	1.6	2.7
			RQ ₉₅	0.4	12.7	5.2	5.1	1.3	2.4

Therefore UV filters not included in this approach due to lack of data, such as OC and BMDMB, but with a high $\log K_{ow}$ and a great presence in sampled beaches, could have more toxic effects in aquatic organisms at lower concentrations. A recent study conducted in zebrafish (*Danio rerio*) has shown that OC affects hematopoiesis, blood flow, blood vessel formation and organ development besides not being able to discard effects on the endocrine system (Blüthgen et al., 2014). Eventually, UV filters are found in the environment as a mixture of several compounds, so joint effects of such mixtures, additive (Heneeweel et al., 2005) or synergic (Kunz and Fent, 2006) effects can be expected and should be quantified in a future ERA. For all these reasons, it is presumed that the environmental risk posed by the determined UV filter levels may be higher than we are able to quantify with this approach.

4. Conclusions

All UV filters under study were detected in seawater samples from six beaches monitored in Gran Canaria Island. UV filter concentrations reached hundreds or thousands of ng/L. OD-PABA was the only compound not detected. A high correlation was observed between OC and BMDMB, which was directly associated with their joint uses in sunscreen formulations. To the best of our knowledge, this is the first study reporting DHHB concentrations in coastal waters.

All beaches under study presented the same UV filter profile, the highest concentrations were determined for OC, BMDMB and BP-3. Significant higher concentrations were determined in "semi-enclosed" beaches (PR, MG and AM). No clear seasonal pattern was established and this fact can be attributed to an intensive use of beaches during all the year.

Finally, as the ERA approach showed, significant potential for adverse effect were found for 4-MBC at CA beach and particularly for EHMC at PR beach.

Acknowledgements

This study was supported by the CARMAC project (MAC/2/C011), co-funded by Programa de Cooperación Transnacional MAC 2007–2013.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.02.054>.

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