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Adverse effects of UV light protection compounds on marine organisms

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Abstract

The growing use of ultraviolet (UV) light protection compounds on a wide range of personal care products (PCPs), plastics, industrial products and textiles has turned them on chemicals of emerging concern, especially for marine habitats. UV compounds can reach marine habitat directly and indirectly via recreational bathing activities or trough discharge from wastewater treatment plants (WWTPs) respectively. The high bioavailability of these compounds makes them hazardous for marine organisms. It has been demonstrated the production of adverse effects of UV compounds on a wide range of marine organisms, from viruses to marine mammals, such as inhibition of body growth and weight, toxicity effects, disturbance on reproduction system, endocrine disruption properties or bleaching on corals. Due to the liphophility, persistence and stability of UV compounds, they bioaccumulate on different species of marine organisms and biomagnificate through food chain via predator-prey interactions. This converts them into harmful contaminants for human health, especially in countries with a high consumption of marine organisms, making necessary a study of their presence on food from local markets.

The purpose of this work is to summarize the adverse effects that UV light protection compounds can produce on marine organisms, their capacity to bioaccumulate and biomagnificate on different species and their toxicity and risk for each type of organism.

Keywords: UV light protection compounds, UV filters, UV stabilizers, marine organism, toxicity, bioaccumulation, biomagnification

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1. Introduction

Currently, anthropogenic contaminants are very harmful for the marine organisms. One of the most recent contaminants studied are UV light protection compounds (UVLPC), who are chemicals of emerging concern specially in marine habitats.

UVLPC can be divided by their purpose on UV filters and UV stabilizers. UV filters can absorb or reflect UV light in the range of UV-A (320-400 nm) and UV-B (290-320 nm) but have null absorption in the visible radiation, while UV stabilizers are added to prevent their degradation. Some of these contaminants are used for both purposes (Apel et al., 2018). UV-A can penetrate into dermis and epidermis causing premature photo-aging, while UV-B induce DNA damage and skin cancer (S. Kim & Choi, 2014). Moreover, UV light produce damage and discolouring in plastic products.

The first UVLPC detected in the environment was a benzophenone type, found on Baltic Sea by Ehrhardt et al, 1982. In the beginning, UVLPC were design for sunscreens products (Montesdeoca-Esponda et al., 2013) as light protection avoiding the effects of UV longer exposures.

The first researches of sunscreens protections were carried out at the end of nineteenth century (Sánchez Rodríguez et al., 2015). Currently, UVLPC have a wide use in PCPs (soap, toothpaste, hair care products, lotions, fragrances, nail polish, lipstick) (Montesdeoca-Esponda et al., 2013, Kaiser et al., 2012), plastics (Kaiser et al., 2012, Wang et al., 2016), industrial products (corrosions inhibitors in dishwater detergents, automotive antifreeze formulations, cooling systems, brake fluids, solid cooling lubricants) (Montesdeoca-Esponda et al., 2013, Wang et al., 2016) or clothing (Kaiser et al., 2012). Gago-Ferrero et al. (2012) estimated that 10000 tons of UVLPC are produced annually.

1.1. Source and distribution of UV light protection compounds on marine environment

UVLPC may enter into the marine habitat through different ways. One of the major sources to marine environment is via discharge of both, domestic and industrial wastewater-treatment plants (WWTPs) (Montesdeoca-Esponda et al., 2013). The range of elimination of UVLPC in WWTP depends on the type of treatment and the physicochemical properties of each compound (Emnet et al., 2015). Sometimes, these compounds are not efficiently removed. Another way to reach marine environments is via recreational activities in coastal waters (Paredes et al., 2014, Sánchez-Quiles & Tovar-Sánchez, 2015), lakes and rivers (Montesdeoca-Esponda et al., 2013) because of their use in sunscreen and other PCPs.

Waters and sediments in places near discharge zones or with high coastal activity, and marine organisms that live there have higher concentration of UVLPC than those that are far away from human activity (Lu et al., 2019). Nonetheless, UVLPC have been detected even in Antarctic oceanic waters (Cadena- Aizaga et al., 2020) in concentration levels that are comparable with those found in other parts of the world, which suggest that these pollutants can be transported by ocean currents or through the atmosphere. Low temperatures, long periods of dark and presence of ice in polar climates, reduce degradation of UVLPC making it more persistent in Antarctic coastal environments

(Emnet et al., 2015). Besides, UVLPC that arrive to Antarctic environments may be transformed in sea ice that contain them. During summer, ice release these kind of compounds and they are transported away to others un-impacted areas via ocean currents, making that all ocean waters could be contaminated (Emnet et al., 2015).

UVLPC have been found in different matrices like rivers and lakes (Gago-Ferrero et al., 2012; Li et al., 2017), wastewaters (Balmer et al., 2005; Emnet et al., 2015; Langford et al., 2015), drinking waters (Li et al., 2017), surface waters (Díaz-Cruz et al., 2008; Emnet et al., 2015; Sánchez Rodríguez et al., 2015; Lu et al., 2016a), sediments (Langford et al., 2015; Lu, et al., 2016a; Apel et al., 2018) and even in sea ice (Emnet et al., 2015). Gago-Ferrero et al. (2012) justify the presence of these contaminants on those matrices because of their poor biodegradability. Generally aqueous matrices contain UVLPC at levels of ng/L to sub- µg/L while solid matrices present sub-ng/g levels (Tsui et al., 2014). Another factor that affects the accumulation of UVLPC in the marine environment is the season of the year; summer is the period that shows highest accumulation due to the increase of coastal activities. For example, it was demonstrated by Sankoda et al. (2015) that octinoxate (EHMC) and octisalate (EHS) concentrations levels are conditioned by seasonal variations. Concentrations of such compounds were found to have a spatial variation depending on the number of recreational bathing activities, which are grater in summer than in winter. Furthermore, the presence of these compounds also shows diurnal variations. These variations appear to be correlated with the number of bathers, being the night the time with less bathers and therefore, the hours with the lowest concentrations.

Finally, the presence of different types and concentrations of UVLPC around the world shows their wide use and the different formulations which are used in each country.

1.2. Bioaccumulation and biomagnification on marine organisms

Not only environmental matrices show hazardous levels of UVLPC. These contaminants can be uptaken by marine organisms via matrices contaminated with them (e.g. water column, sediments or even microplastics) or they may be absorbed to the surface of microorganisms (Nakata et al., 2009; Sánchez-Quiles & Tóvar-Sánchez, 2015). For this reason, benthic fauna is more exposed to UVLPC than pelagic organism since sediments are one of the major reserves of these compounds (Kaiser et al., 2012; Lu, et al., 2016a).

UVLPC are not harmful only for organisms, but also for human health since our diet could include some of these organisms. Cunha et al. (2018) investigated the presence of some of these compounds in commercialized seafood, finding high concentrations of 4-Methylbenzylidene camphor (4-MBC) (56, 2 µg/Kg dry weight (d.w.)) on wild mussels. Benzophenone 1 (BP-1) and benzophenone-3 (BP-3) were also found frequently. Octocrylene (OC) on farmed seabream was the most contaminant compound on seafood, with levels of 103,3 µg/Kg d.w. Other compounds like EHMC, EHS, Homosalate (HMS) and Amiloxate (IMC) were detected but in lower frequency. The most affected commercialized seafood by UVLPC was farmer seabream, while the less affected were octopus, sole and crabs. The authors highlighted the importance of the results, especially for countries with high consumption of seafood such as Portugal and Spain.

Due to the lipophilicity, persistence and stability of some UVLPC, they bioaccumulate on marine organisms and biomagnificate through the food chain reaching marine mammals levels (Montesdeoca-Esponda et al., 2013). Bioaccumulation depends on many factors such as size, age, sex, diet, metabolic activity, habitat, proteins and lipids content in tissues and muscles, seasons, feeding, growth and reproduction rates, migrations, etc. (Gago-Ferrero et al., 2012). Toxic kinetics of these chemicals, their biotransformation capacity as well as the proximity to the source are also factors that affects to their accumulation in marine organisms (Lu et al., 2019).

Marine organism store UVLPC directly from the surrounding environment or incorporate them from their diet (Gago-Ferrero et al., 2015). Nakata et al. (2009) showed that bioaccumulation varies depending on the capacity of retention and metabolism of each specie, suggesting that bioaccumulation has a positive correlation between concentration of the contaminant and the trophic status of organism in marine ecosystems. The most affected organisms by bioaccumulation are mussels and fish (Gago-Ferrero et al., 2012). For this reason, some species of mussels and fish have been used such as indicators of the levels of these contaminants in waters.

1.3. Official regulation of UV light protection compounds

Due to the grade of toxicity that many investigations have shown, the UVLPC permitted in PCPs and his concentrations have been regulated by local or international agencies (Sánchez-Quiles & Tovar-Sánchez, 2015). Around 45 UVLPC are subjected to regulation on different countries (Tovar-Sánchez et al., 2013).

In Europe, 27 UVLPC are allowed be used on cosmetics, while USA only allows 16 UV of them, 26 in Australia and 31 in Japan (Wang et al., 2016; Cunha et al., 2018; Cadena-Aizaga et al., 2020).

Maximum level of some UVLPC allowed on commercial products in Europe is: 10% of BP-3, 5% of benzophenone 4 (BP-4), 10% of EHMC, 10% of OC, 8% of 2-Ethylhexyl 4-(dimethylamino) benzoate (OD-PABA) and 4% of 4-MBC. Meanwhile, the limits stablished in USA are: 6% of BP-3, 10% of BP-4, 10% of EHMC, 10% of OC and 8% of OD-PABA, while 4-MBC is banned (Paredes et al., 2014; Langford et al., 2015; Vidal-Liñán et al., 2018).

In the same way, in Japan, 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV-327) has been regulated due to its high bioaccumulation properties (Kim, et al., 2011a, Nakata et al., 2010) while UV-320 has been banned in 2007. However, most recent studies have shown the presence of this compound in Japanese waters (Nakata et al., 2009). Also, a percentage of 5% is the maximum allowed for BP-3 in Korea (S.Kim & Choi, 2014).

Taking into account all above mentioned, the aim of this final master degree work is to gather and summarize the information published since 2000 about how UVLPC affect to different types of marine organisms, its bioaccumulation and biomagnification, ecotoxicity and risk in the marine environment. Moreover, this overview aims to find some potential future needs in this field.

2. Classification of UV compounds

The UVLPC can be classified onto two types depending on their mechanisms of action: organic and inorganic UVLPC.

2.1. Organic UV light protection compounds

Organic light protection compounds absorb UV radiation with excitation to higher energy state (Gago-Ferrero et al., 2012). They are slightly soluble and can change in water matrices. Commercial products use mostly geometrical (*E*) isomers but some UVLPC have both (*E*) and (*Z*) isomers (Gago-Ferrero et al., 2012). They can suffer photodegradation by photolysis or photoisomerization and generate reactive oxygen species, which can harm the health of marine animals (Sánchez-Quiles & Tovar-Sánchez, 2015). Photolysis occurs when the absorbing molecule dissociates into reactive fragments or reactive intermediates and it may be direct or indirect, while photoisomerization generate chemical compounds that absorb less UV light than their parents (Díaz-Cruz et al., 2008).

Properties of each compound may change depending on his octanol-water partition coefficient (K_{ow}). UVLPC with K_{ow} <1 are hydrophilic, with K_{ow}> 4 are hydrophobic, with K_{ow} >8 are not considered readily bioavailable and with K_{ow} >10 are considered not bioavailable at all (Cadena-Aizaga et al., 2020).

Organic light protection compounds can be classified by their structure depending on their chemical family and physicochemical properties, being the most common the *benzotriazole UV stabilizers (BUVSs), benzophenones (BP), camphor derivatives and cinnamate derivatives.*

BUVSs are derivates of benzotriazole, which have phenolic group attached to the structure (Montesdeoca-Esponda et al., 2013). These compounds are very weak acids which exist in the environment in their neutral forms (Lu, et al., 2016a) and they can absorb the full spectrum of UV light (UV-A and UV-B). The most employed BUVSs (Table 1) are; UV-P (2-(benzotriazol-2-yl)-4-methylphenol), UV-9 (2-(2H-Benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol), UV-234 (2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol), UV-320 (2-(2'-hydroxy-3-5-di-tert-butylphenyl)benzotriazole), UV-326 (2-tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol), UV-327 (2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol, UV-328 (2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol), UV-329 (2-(benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl) phenol), UV-350 (2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol), UV-571 (2-(2H-Benzotriazol-2-yl)-6-dodecyl-4-methylphenol), UV-360 (2,2-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol] and BZT (1-H-benzotriazole). Half-life time for UV-234, UV-326, UV-327, UV-328, UV-329 and UV-350 in matrices like water and sediments ranging between 60 to 542 days respectively, which converts BUVSs onto contaminants with high persistence in the environment (Lu, et al., 2016a).

The most employed BP type (Table 1) are: BP-1 ((2,4-dihydroxyphenyl)(phenyl)methanone), BP-2 (2,2',4,4'-Tetrahydroxybenzophenone), BP-3 (2-Hydroxy-4-Methoxybenzophenone), BP-4 (5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid), BP-8 (2,2'-Dihydroxy-4-Methoxybenzophenone), THB (2,3,4-trihydroxybenzophenone), 4-HB (4-hydroxybenzophenone) and 4-DHB (4,4-dihydroxybenzophenone). BP-1, BP-8 and THB are transformed metabolite from BP-3 (S.Kim & Choi, 2014). BP-1 is produced in oxic conditions as a biodegradation product of BP-3. This compound has longer biological half-life and higher estrogenic potency than BP-3, which makes it one of the major metabolites of BP-3 on fish.

Camphor derivatives are also effective UVB-absorbers. This type of compounds can be easily bioaccumulated in tissues of organisms (Wang et al., 2016). The most employed are: 4-MBC (4-methylbenzylidene camphor) and 3-BC (3-benzylidene camphor) (Table 1).

Cinnamate derivatives have a special bond that make these compounds absorb better the 305 nm wavelength (Wang et al., 2016). The most employed (Table 1) are: OMC (2-Ethylhexyl 4-methoxycinnamate), OC (2-Ethylhexyl 2-cyano-3,3-diphenylacrylate), EHMC (2-Ethylhexyl 4-methoxycinnamate), EHS (2-Ethylhexyl salicylate), HMS (3,3,5-Trimethylcyclohexyl Salicytale), IMC (Isoamyl 4-methoxycinnamate 3-methylbutyl (E)-3-(4-methoxypenyl)prop-2-enoate), PABA (4-aminobenzoate) OD-PABA (2-Ethylhexyl 4-(dimethylamino) benzoate), Et-PABA (Ethyl-4-aminobenzoate), BS (Benzyl salicylate) and PS (Phenyl salicylate). Et-PABA is the ethyl ester of PABA and is used as a substitute of this in sunscreens and as an anaesthetic in veterinary medicine. Second compound with the most occurrence in waters around the world is OMC, being China, Spain and Japan the countries with the highest levels reported (4043 ng/L, 1200 ng/L and 1080 ng/L, respectively). OMC is also a recurrent compound in sediments matrices (Cadena-Aizaga et al., 2020).

2.2. Inorganic UV compounds

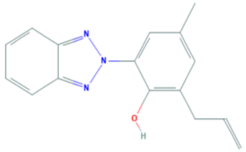
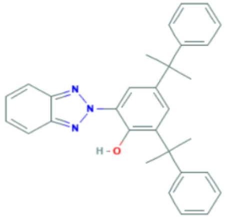
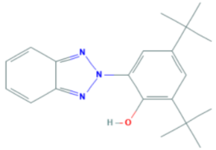
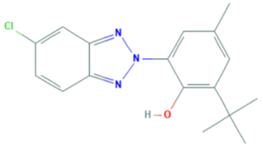
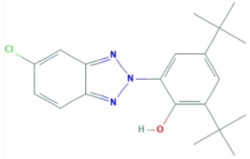
Inorganic UVLPC can reflect, scatter and absorb UV radiation and are essentially titanium dioxide (TiO_2) and zinc oxide (ZnO) (Table 1). These compounds have high effectivity against UV radiation and their use is authorized in the order of nanoparticles (Sánchez-Quiles & Tovar-Sánchez., 2015). The problem with TiO_2 is the size of the particle used on sunscreens, because the nanoparticles of this compound have higher toxicity due to its higher surface area per particle, increasing therefore its reactivity (Chen et al., 2011).

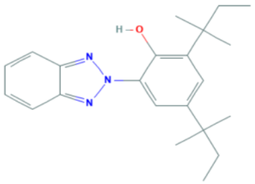
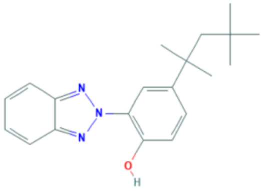
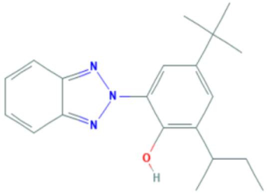
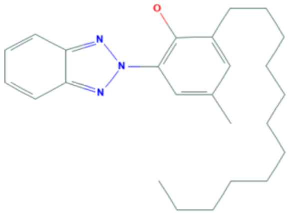
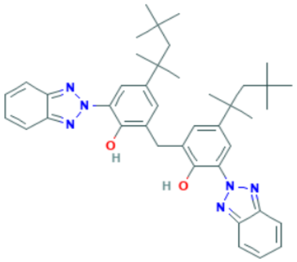
Organic and inorganic light protection compound mixed are commonly used to increase the spectrum of protection on sunscreens (Sánchez-Quiles & Tovar-Sánchez., 2015).

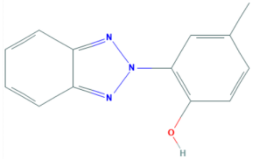
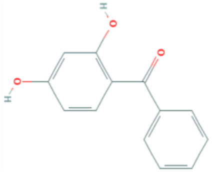
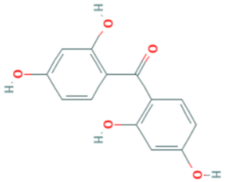
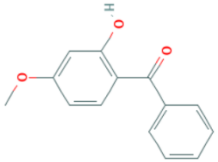
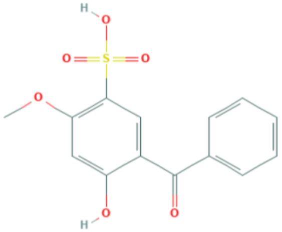
3. Presence and effects of UV light protection compounds on marine organisms

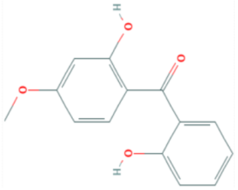
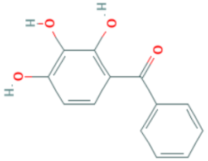
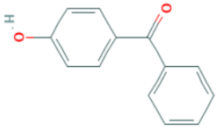
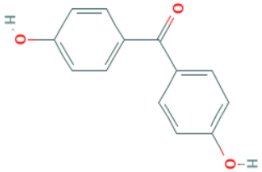
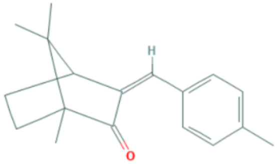
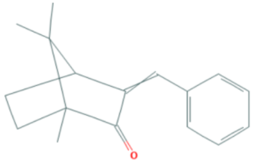
As it was mentioned above, recent studies have shown the risk and negative effects that UVLPC have on marine organisms. Relationship between the growing occurrence of these compounds and their negative effects on marine biota has been reported by different authors (Cadena-Aizaga et al., 2020). In the following section these adverse effects are reviewed and summarize for important types of marine organisms: viruses and bacteria, algae, small invertebrates, fish and marine mammals.

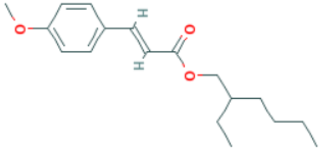
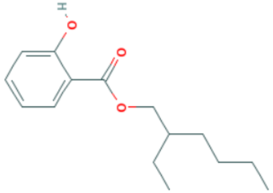
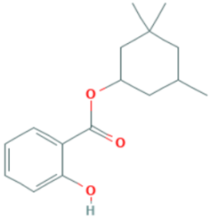
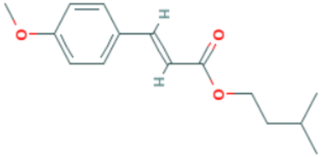
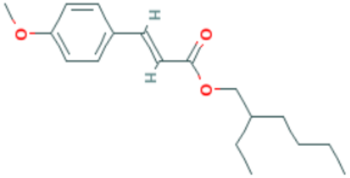
Table 1. List of the most commons organic and inorganic UV light protection compounds used, with their CAS number, chemical structure, Log $K_{ow,}$ molecular weight and solubility in water. Data obtained from the National Center for Biotechnology Information PubChem (https://pubchem.ncbi.nlm.nih.gov/).

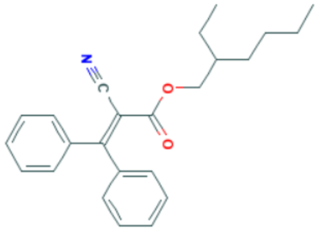
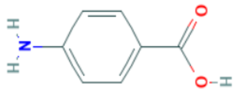
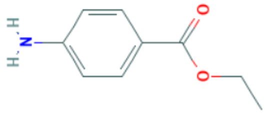
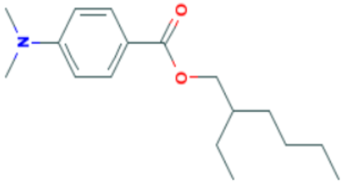
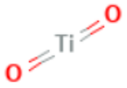
Chemical Name (INCI*)	**CAS no.**	**Structure**	**Log K_{ow}**	**Molecular weight (g/mol)**	**Solubility (g/L)**
Benzotriazole UV stabilizers (BUVSs)					
UV-9	2170-39-0		5.4	265.31	-
UV-234	70321-86-7		8.6	447.58	-
UV-320	3846-71-7		7.21	323.44	-
UV-326	3896-11-05		5.6	315.8	-
UV-327	3864-99-1		6.9	357.88	-

UV-328	25973-55-1		7.4	351.49	-
UV-329	3147-75-9		7.3	323.43	-
UV-350	36437-37-3		6.3	323.4	-
UV-571	125304-04-3		8.95	393.56	-
UV-360	103597-45-1		12.8	658.87	-

UV-P	2440-22-4		4.3	225.25	-
Benzophenone (BP)					
BP-1	131-56-6		3.2	214.22	0.39
BP-2	131-55-5		2.4	246.21	0.98
BP-3	131-57-7		3.6	228.24	0.1
BP-4	4065-45-6		2.2	308.31	11

BP-8	131-53-3		3.3	244.24	-
THB	1143-72-2		2.8	230.22	-
4-HB	1137–42–4		3.1	198.22	-
4-DHB	611-99-4		2.7	214.22	0.6
Camphor Derivatives					
4MBC	36861-47-9		4.5	254.4	0.017
3BC	15087-24-8		4.1	240.34	0.034

Cinnamate Derivatives					
EHMC	5466-77-3		53	290.4	0.0064
EHS	118-60-5		5.7	250.33	-
HMS	118-56-9		5	262.35	0.021
IMC	71617-10-2		3.9	248.32	-
OMC	5466-77-3		5.3	290.41	-

OC	6197-30-4		7.1	361.5	0.00036
PABA	150-13-0		0.83	137.14	9.15
Et-PABA	94-09-7		1.86	165.19	1.31
OD-PABA	21245-02-3		5	277.4	0.0047
Inorganic UV Compounds					
TiO2			-	79.87	-
ZnO			-	81.4	-

*INCI (International Nomenclature for Cosmetic Ingredient).

- : Data not found

3.1.Viruses and bacteria

Sunscreen products affect microbial community structure increasing bacterial abundance and having a significant impact on its enzymatic activities (Danovaro & Corinaldesi., 2003). Moreover, UVLPC may alter the N, P and C cycle, raising the N and P cycles and reducing C mobilization. Bacteria are more sensitive to polar BP compounds, and Liu et al. (2015) found that toxicity on bacteria *Photobacterium phosphoreum* increases with the number of hydroxyl groups on the benzene rings. It has been also detected that 4DHB and Et-PABA causes acute toxicity on bacteria *Vibrio fischeri* (Molins-Delgado et al., 2016).

Moreover, the presence of these contaminants increases viruses abundance, which indicates the presence of substances inducing prophages. Furthermore, OMC, BP-3 and 4-MBC cause coral bleaching due to viral infections (Danovaro et al., 2008). These compounds cause a large amount of mucous and, as it can be seen in Figure 1, the decolouring of the coral by damaging the symbiotic zooxanthellae. Around 10% of coral reefs in the world are threatened by sunscreens products (Danovaro et al., 2008.). The fact that sunscreens affect to coral is very dangerous, because coral reefs are the ecosystem that produce most biodiversity. Thus, in some countries several ingredients of sunscreens have been banned due to this reason.

3.2.Algae

Spray sunscreens solutions content more hydrosoluble compounds than cream solutions, making them more bio-available to phytoplankton (Tovar-Sánchez et al., 2013). Concentrations of UVLPC on algae may vary depending on the season of the year.

It has been demonstrated by Paredes et al. (2014) that BP-3, BP-4 and EHMC are toxic for *Isochrysis galbana,* being BP-3 the most toxic compound at concentrations as low as ng/mL. According to the EC_{50} (concentration causing toxic effects in 50% of the organisms tested) values, the toxicity of these three compounds, is similar to that reported for the most toxic trace metals. Furthermore, comparing the effect of these contaminants in three species of invertebrates, *Isochrysis galbana* showed be the organism most affected by UVLPC. Also, some of these compounds like BP-1, EHMC and OD-PABA may inhibit growth on some specific algae like *Raphidocelis subcapitata* (Molins-Delgado et al., 2016).

3.3.Small invertebrates

More than 90% of animal species are invertebrates. These organisms are susceptible of being affected by lipophilic substances because of their life habits. For example, a decrease on reproduction and an increase of mortality is caused by 3-BC and 4-MBC on *Potamopyrus antipodarum* and *Lumbriculus variegates* while EHMC has toxic reproduction effects on *Melanoides tuberculate* (Schmitt et al, 2008; Kaiser et al., 2012). Invertebrate species are preferred food for most kind of fish and other organisms from higher trophic levels, which makes that BUVSs can be accumulated on significative concentrations at the highest trophic levels (Kim et al., 2011a).

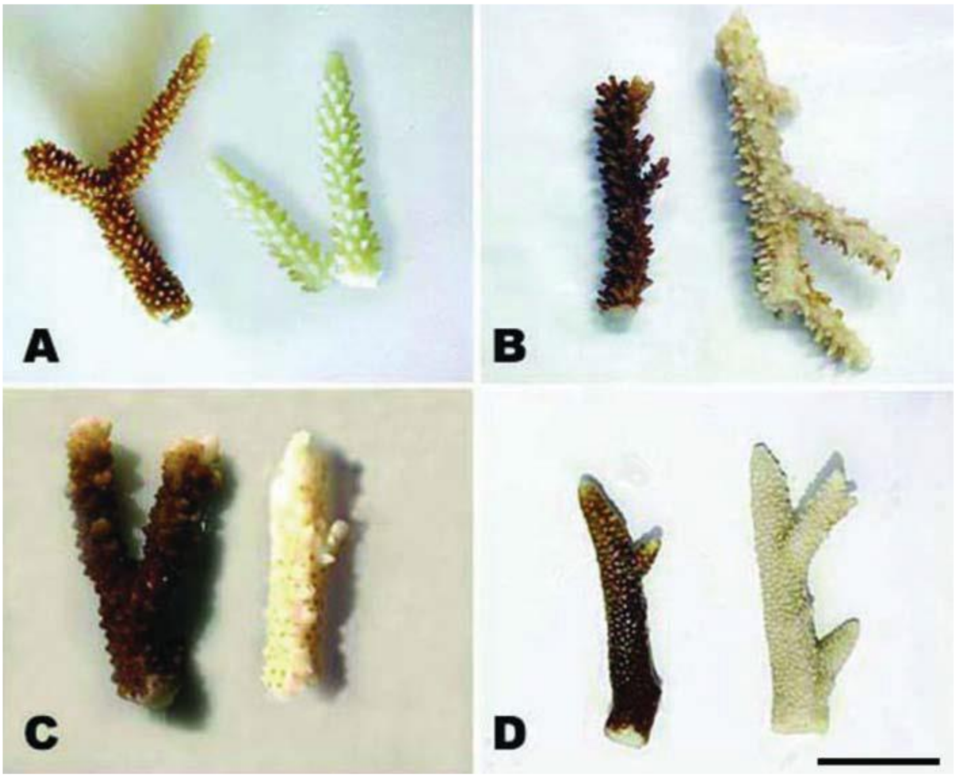


Fig 1. Decolouring of coral after sunscreens exposition experiment: untreated (brown) and treated (white) nubbins after 72 h: *Acropora cervicornis* (A); *Acropora divaricata* (B); *Acropora sp.* (C); and *Acropora intermedia* (D). Scale bar= 2cm. Images taken from Danovaro et al., 2008.

Presence of UVLPC in crustaceans has been demonstrated and studied. Preference of crayfish for the sediments as its habitat makes *Orconectes spp* has presented high levels of UV-328 and UV-350 (Lu, et al., 2016a). Different researches in which toxicity of several UVLPC has been investigated in different species have shown that UV-571, BP-3, BP-1 and BP-8 produces acute toxicity on *Daphia pulex* (Kim et al., 2011a), while BP-3, BP-4, EHMC, 4-MBC and 4HB affect to *Daphia magna* decreasing the length on adults (Liu et al., 2015; Molins-Delgado et al., 2016; Sieratowicz et al.,2011). Additionally, a study about toxicity of UV filters on *Daphia magna* showed that 3-BC also decrease the number of offspring and delay the time to first reproduction (Sieratowicz et al., 2011). Furthermore, a research about combined ecotoxicity of UV filters detected that BP-1, BP-3, 4MBC and EHMC interact between them modifying their toxicity on crustaceans, being lower when they are in mixture because of antagonist effects (Molins-Delgado et al., 2016). Also, the same authors reported that the toxicity of some BP compounds (BP-1, BP-3, BP-4, 4-HB, Et-PABA, EHMC, 4-MBC and BZT) in *Daphia magna* is due to hydrophobicity being higher the toxic effect the lower solubility of the compound (Molins-Delgado et al., 2016).

Marine mussels are the main object of the studies of UVLPC on invertebrates. The most contaminated mussels were detected in places with a lot of recreational human activities, mainly near to WWTPs effluents and on beaches with close structure where water exchange was lower causing lower dilution of contaminants. It has been demonstrated that mussels incorporate EHMC, OCT and OD-PABA through bathing activities. Highest concentrations of these compounds were found on mussels from

Portuguese and French coasts (Bachelot et al., 2012; Picor Groz et al., 2014). Studies carried out in soft tissue of clams showed that it is capable to store BP-3, UV-320, UV-326 and UV-327 (Emnet et al., 2015; Nakata et al., 2009). Also UV-326, UV-327 and UV-328 has been detected on oyster tissues showing only bioaccumulation of UV-326. (Nakata et al., 2009). More specifically, a study about bioaccumulation in *Mytilus galloprovincialis* detected a very quick uptake of 4-MBC and BP-4 while BP-3 and OD-PABA had lower incorporation. Moreover, *M. galloprovincialis* can biotransforms OD-PABA, decreasing the levels on its tissues (Vidal-Liñán et al., 2018). Nakata et al. (2009) found UV-328 in flat gastropods at concentrations of 460 ng/g.

Paredes et al. (2014) analysed the effects of different UVLPC on species of different trophic levels. Most toxic UVLPC for *Mytilus galloprovincialis* was 4-MBC, followed by EHMC and BP-3. In contrast, larvae of *Paracentolus lividus* resulted to be more sensitive to EHMC and 4-MBC than to BP-3. Something similar occurs with *Siriella armata*, which was more affected by 4-MBC and EHMC than by BP-3. Summarizing, the most toxic UVLPC for marine invertebrates EHMC and 4-MBC, whereas BP-4 was the least toxic. Furthermore, toxic levels of UVLPC are comparable to those found for the most toxic trace metals.

3.4.Fish

Fish is the species family which most research about adverse effects of UVLPC s have been carried out. The first research was made by Nagtegaal et al. (1997), who demonstrates the presence of seven UV filters in *Perca fluvialis* and *Rutilus rutilus*. In addition, they discovered the variable selectivity of UV filters which bioaccumulate in different species and in their body parts. It has been demonstrated that the nearest the fish species was from the most contaminated sediments, the greater was the concentrations levels of the UVLPC on their bodies. Moreover, fish samples presented higher levels of contaminants than sediments, showing bioaccumulation and biomagnification of these compounds (Gago-Ferrero et al., 2015).

3.4.1. BUVSs

Talking about BUVSs, UV-328 accumulates at high concentrations on blood plasma of carp fish, gizzard shard, brown bulhead (Lu et al., 2019), indian anchovy, common ponyfish, bumpnose trevally, flathead grey mullet (Kim et al., 2011b), white sucker (Lu, et al., 2016b) and hammerhead sharks (Nakata et al., 2009) and on bream liver (Wick et al., 2016;). The wide variety of species in which has been detected these compound shows the high availability and the easily uptake by different fish species. UV-234 was found in hornyhead chub (*Nocomis biguttatus),* common shiner (*Luxilus cornutus),* northern pike (*Esox Lucius)* and white sucker (*Catostomus commersonii)* on higher concentrations than levels found in benthic species, suggesting the preference of UV-234 to remain in water column instead to accumulate in sediments. (Lu, et al., 2016b; Lu et al., 2019). Furthermore, it has been found that UV-234 can be bioaccumulated in fish while the organism grows. Nevertheless, this compound was found at lower concentrations on rock bass, which may suggest the diverse preferences of each specie to uptake different UVLPC. Also, UV-327 was detected in blood plasma from northern pike (*Esox Lucius)* and on liver from bream (*Abramis brama),* Japanese mullets and seabass

(Nakata et al., 2009; Lu, et al., 2016b; Wick et al., 2016). Figure 2 represents different concentrations of BUVSs in fishes from Manila Bay (Philippines) and as it can be seen, UV-328, UV-P, UV-320 and UV234 were the most frequently compounds found, in the 88%, 86%, 79% and 55% of the analysed samples, respectively (Kim et al., 2011b). Most interesting is that even in fishes belonging to the same family, compositions of BUVSs detected in their tissues were different, which suggest that concentrations levels of accumulation of BUVSs is quite specific.

3.4.2. BP types and camphor derivates

BP type UVLPC has also been widely studied in fish. Fish liver is preferent tissue to store BP-3 (Emnet et al., 2015). Confirming this, Figure 3 shows concentrations of some UV filters in cod liver; BP-3 was also detected at high levels on liver from Northen shrimp (*Pandalus borealis)* and Atlantic cod (*Gadus morhua)* (Langford et al., 2015). Futhermore, its presence has been detected on fish from lakes and rivers (Balmer et al., 2004; Balmer et al., 2005; Zenker et al., 2008; Gago-Ferrero et al., 2015). Bioaccumulation of this compound it has also been demonstrated for perch and roach (Gago-Ferrero et al., 2012).

OC has been found on fish tissues at high concentrations; thus, it has been detected in brown trout, roach, cod liver, river fish (*Silurus glanis)* (Balmer et al., 2004; Díaz-Cruz et al., 2008¸ Gago-Ferrero et al; 2015). Another interesting effect is that fish from rivers has higher availability of the compound compared with lakes fish, suggesting a higher bioaccumulation in that kind of organims than in lake fish or lesser metabolization of this compound on river species (Buser et al., 2006).

In the same way, 4-MBC was found on fish tissues at high concentrations (Balmer et al., 2004). Furthermore, 4 -MBC can be selectively accumulated; for example, 4-MBC is accumulated by perch in muscle while roach accumulates it in offal (Gago-Ferrero et al., 2012). Brown trout (*Barbus graellsii)* also accumulates 4-MBC on its tissues (Díaz-Cruz et al., 2008; Gago-Ferrero et al., 2015).

Other compounds like EHMC and HMS can also be selectively accumulated. Thus, the presence of EHMC has been detected on fish from lakes such as white lake fish (*Coreous sp.)*, barb (*Barbus barbus)* and chub (*Leucisus cephalus)* (Balmer et al., 2004; Balmer et.al, 2005, Zenker et al., 2008). Also, it has been reported the presence of high leves of this compound on the river fish *Silurus glanis* (Gago-Ferrero et al., 2015). On your part HMS is accumulated in offal by perch and in muscle by roach. These two species have shown bioaccumulation of these compound (Gago-Ferrero et al., 2012). Furthermore, *Danio rerio* suffers developmental effects such as impaired blood circulation, a decrease on its hearbeat and oedema when it is exposed to EHMC (Kaiser et al., 2012).

The most common effect of UVLPC on marine organism is their potential endocrine disruption. Depending on the UVLPC analysed, they could possess different effects on marine organisms such as antiestrogenic activity, androgenic activity and antiandrogen activity (Brausch & Rand., 2011). For example, disappearance of tubercles in male fish suggest a potential estrogenic effect while formation of tubercles in female fish is an indicator of potential androgenic effect (Weisbrod et al., 2007). Furthermore, it has been shown additive activity between some UVLPC mixtures due to synergic interactions, (e.g. some UVLPC may increase estrogenic activities caused by other compounds present in the mixture) (Fent et al., 2008).

Many BP type UVLPC are endocrine disruptors, causing estrogenic effects on fish (Wang et al., 2016). BP-2 and BP-3 have estrogenic effects on reproduction on fish, significant VTG and induced dose-dependent effects on gonad histology of females and males and secondary sex characteristics (Kunz et al., 2006; Weisbrod et al., 2007; Fent et al., 2008; Kinnberg et al., 2015; Wang et al., 2016). BP-3 produces estrogenic and/or antiandrogen activity on zebrafish *Danio rerio* by change its sex ratio and changing the maturation stages of gonads (Kunz & Fent., 2006; Kinnberg et al., 2015). BP-1 also showed estrogenic and antiandrogenic activity on fish (Kunz & Fent., 2006) and the survival rates started to be affected at concentrations of 4919 µg/L.

It is reported that 4-MBC and 3-BC camphor derivate show anti-estrogenic activity in fish and OMC causes endocrine disruptions (Wang et al., 2016). 3-BC also decreases male secondary sex characteristics and spawning activity due to gonadal degeneration while in females causes a reduction in the number of ovaries and increases ether atretic follicles (Fent et al., 2008). Other adverse effects on fish observed for 4-MBC and 3-BC was a reduction on length gain, weight gain and body length (Kunz et al., 2006). Also, it is demonstrated that Et-PABA has estrogenic effect at high concentrations (4919 µg/L), having VTG induction on fish (Kunz & Fent., 2006; Li et al., 2017).

Finally, it is important to know the contamination levels of these UVLPC in fish related to our diet. Peng et al. (2015), made a comparison of the content on UVLPC between wild and farmed animals. BP-3 and UV-P were detected on both types of organisms at concentrations levels of ng/g. The highest concentrations of 4-MBC were found on red snapper from marine farmer. This organism also stores UV-351, UV-326, UV-234, UV-327 and UV-328 on filet. These results indicate that farmer organisms are more exposed to BUVSs than wild organism which are more exposed to BP-3 and UV-P.

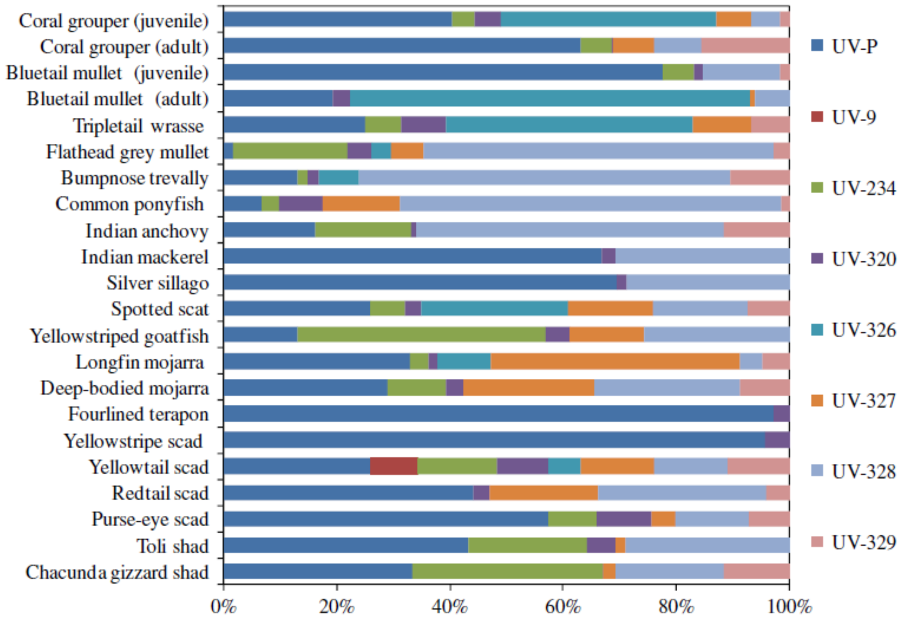


Figure 2. Distribution of different levels of BUVSs in fishes from Manila Bay, Philippines. Figure taken from Kim et al., 2011b.

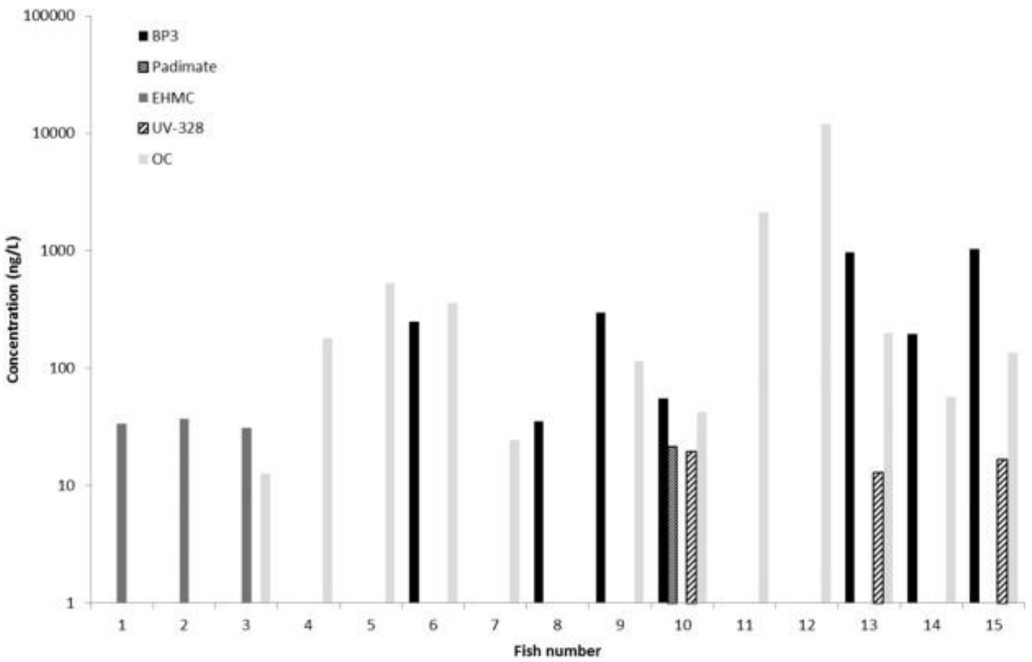


Figure 3.-. Concentrations of UV filters in cod liver (ng/g wet weight). Figure taken from Langford et al., 2015.

3.4.3. Inorganic compounds

Inorganic compounds have been also investigated on fish. TiO_2 decreases body weight, increases gill weight and has effects on liver, brain and heart tissues in a time-dependent manner on zebrafish *Danio rerio* (Chen et al., 2011). The presence of TiO_2 on brain and heart shows that the compound has the capacity to transfer through blood barriers. High concentrations of this compound (7 mg/L) can cause even hypoxia effects as well as loss of balance and body tremor till organism die.

Nevertheless, another research about TiO_2 on rainbow trout (*Oncorynchus mykiss)* did not show mortality effects, but it causes respiratory distress, changes on K, Mn, Zn and Cu levels and a decrease in Na^+ K^+-ATPase activity on gills and brain in a concentration-dependent trend (Federici et al., 2007). Figure 4 shows how exposure to TiO_2 increase the frequency of oedema, an incidence of aneurisms in the secondary lamellae, changes in mucocyte morphology, and hyperplasia in the primary lamellae.

3.5. Marine Mammals

It is important to study the effects of UVLPC in marine mammals to know the biomagnification factor of these contaminants. The most commonly organisms studied to show these effects on marine mammals are dolphins. The reason is because dolphins are sensible to accumulate contaminants, especially in blood plasma (Lu et al., 2019). Interactions between BUVSs and circulating proteins makes blood plasma a reservoir for these type of compounds (Lu et al., 2016b). UVLPC compounds are transfer to marine

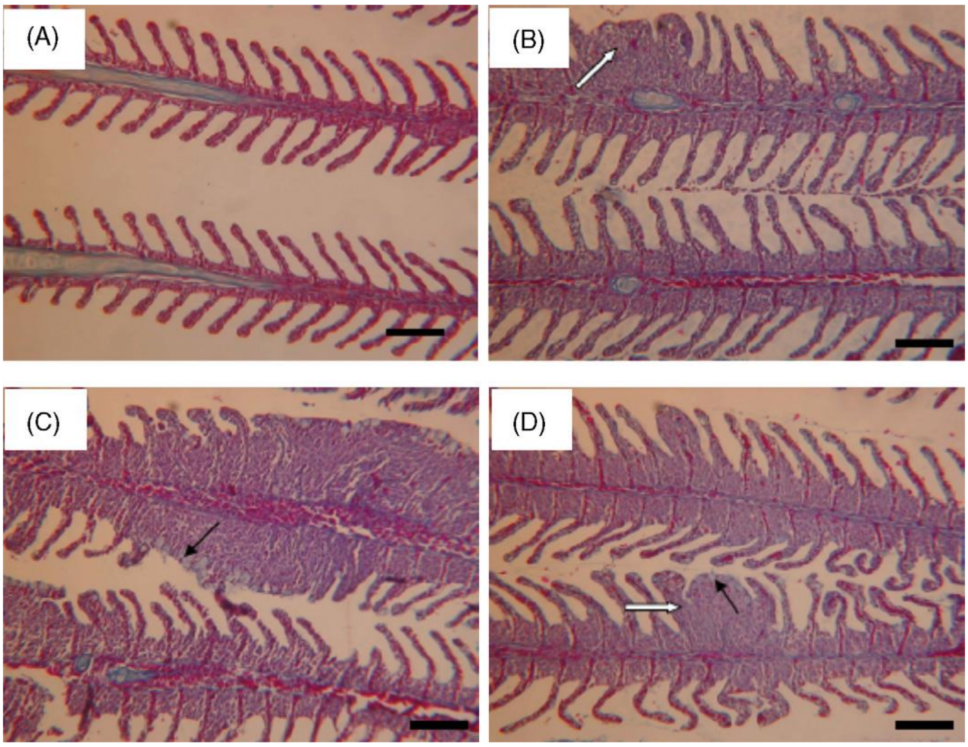


Figure 4. Gill morphology in trout after 14 days of exposure to (A) 0, (B) 0.1, (C) 0.5 and (D) 1 mg/L of TiO_2 nanoparticles. Some oedema of some secondary lamellae is present in B and D treatments (white arrows). C and D treatments show swollen mucocytes (black arrows). Also, fish exposed to TiO_2 nanoparticles present thickening of the primary lamellae. Scale bar = 8 µm. Figure taken from Federici et al., 2007.

mammals offspring by oral administration during pre and postnatal life. These contaminants may affect the central nervous system and reproductive organs of the offspring, making changes in gene expression on its organs and regions of the brain related to sexual dimorphism (Alonso et al., 2015). Some of the levels found of UVLPC in maternal blubber and muscle were similar to PCBs contaminants (Alonso et al., 2015).

On Franciscana dolphins (*Pontoporia blainvillei)* 4MBC, EHMC, OD-PABA and OCT were also detected. Furthermore, OCT was found in breast milk and placenta, suggesting gestational transfer of these UVLPC. Concentrations of OCT in maternal blubber and muscle were 55,8 ng/g lw and 381,7 ng/g lw respectively, while in fetal blubber and muscle were 126,3 ng/g lw and 4108 ng/g lw, respectively, which indicates higher bioaccumulation on fetus than adults (Alonso et al., 2015; Gago-Ferrero et al., 2013). In contrast, as it can be seen in Figure 5, Guiana dolphins have higher levels of UV compounds in adults than in fetus. UV-328 and UV-329 were detected on bottle nosedolphin *(Tursiops truncates)* (Lu, et al., 2016b; Lu et al., 2019). UV-327 and UV-328 were also detected on blubber of finless porpoises (*Neophocaena phocaenoides)* tissues (Nakata et al., 2010).

Another important aspect of interest is the study of the potential endocrine disruption of UVLPC on mammals; thus snapping turtles are quite sensitive due to the sensitivity of their reproductive and growth development. Lu et al. (2019), did not find UVLPC in their blood plasma, but they did not discard the possibility that other UVLPC that they did not studied could be found in turtles blood plasma.

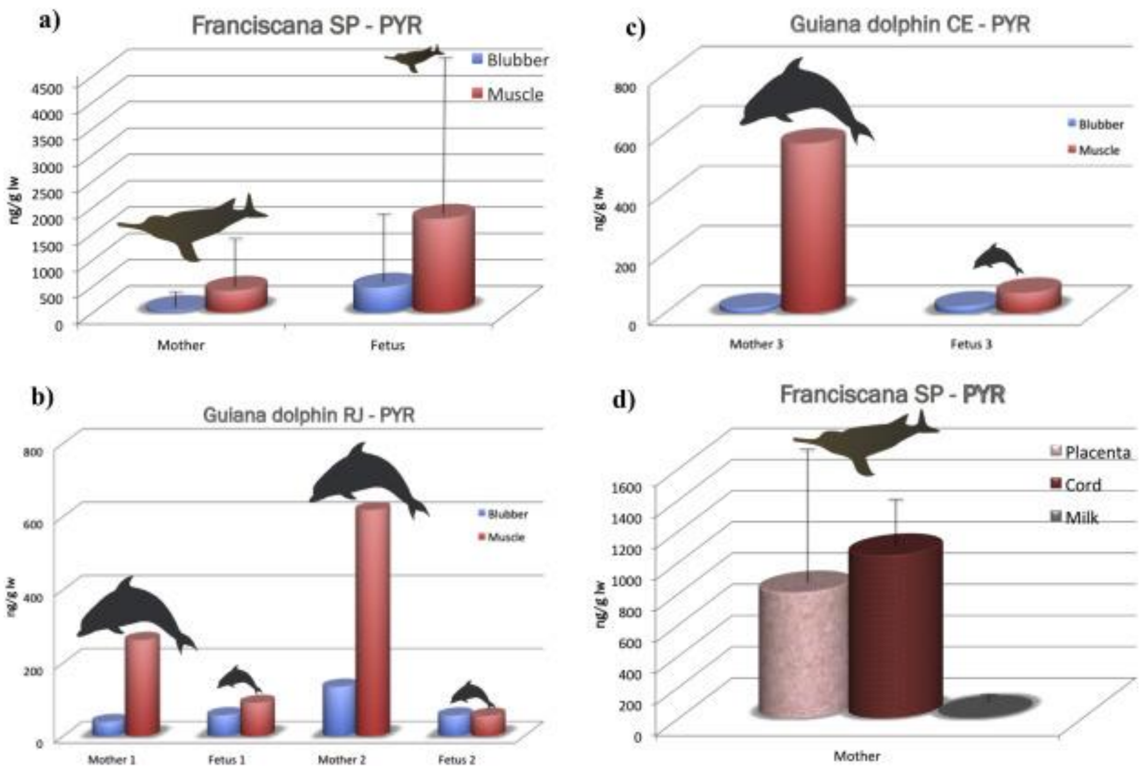


Figure 5. ΣUV filters concentrations in maternal and fetal blubber and muscle of: (A) Franciscanas dolphins from Baixada Santista (SP); (B) Guiana dolphins from Sepetiba bay (RJ); (C) Guiana dolphins from Canoa Quebrada (CE). (D) represents ΣUV filters concentrations in placenta milk of Francisana dolphins from Sao Paulo. Figure taken from Alonso et al., 2015.

4. Conclusions and future trends

UVLPC are a new class of contaminants of emerging concern due to their growing production and usage on different products. This continuous production rising along with the increase of human recreational bathing activities makes these contaminants pseudo-persistent in the environment and their concentrations will increase in the future. Moreover, UVLPC may be transported by ocean currents around the world, promoting their presence on the different marine ecosystems.

Organisms can store this kind of compounds on their tissues and/or muscles due to the lipophilicity, persistence and stability of some of them, producing bioaccumulation into their body and causing biomagnification through the food chain. This makes UVLPC not only harmful for marine species health but also for human health since our diet can include these types of animals.

Different types of UVLPC have been detected around the world on a wide range of concentrations, showing the varied use of them in different countries. They can be found on diverse matrices such as rivers, lakes, wastewaters, coastal waters, sediments, marine biota and even in ice. Among all of them, sediments is the matrix with the highest concentration levels of these contaminants which makes benthic fauna more exposed to them than pelagic organisms. Also, it has been demonstrated that marine organisms are able to store UVLPC into different tissues and muscles depending on the specie. In fish, liver is the preferred tissue to analyse along with muscles while in marine mammals the most frequent matrix to detect these compounds is blood plasma.

Studies about adverse effects of UVLPC have been carried out in a wide type of marine organisms, from viruses to mammals. Among all the studied compounds, 4-MBC, BP-3 and EHMC are the most frequently detected, which suggest how widespread is their use through the world. UV-328 is the BUVS compound most commonly investigated. In fish, this family of compounds is accumulated mainly in liver and their excretion is very limited, suggesting bioaccumulation of them. Marine organisms have higher sensitive for the most lipophilic UV compounds, being an important factor to determinate the toxicity of these contaminants on different species. Also, it is important to have in consideration the transformation products from the UV compounds, that may suppose another source of toxicity on marine environment.

The most outstanding toxic effects of UV compounds on marine organisms are the VTG induction, alteration of body growth, length and reproduction system and decrease of survival rates, even causing mortality in some cases.

Most investigations about the effects of UV compounds on the lowest part of the food chain should be carried out due to these organisms are exposed to highly contaminated matrices and later they are the prey of many other species.

Because of the very low concentration levels of UV compounds in biota, a common drawback of the analytical method to detect them is the contamination background, which requires to have selective and sensitive techniques. Nevertheless, the growing interest on these compounds and the effects on marine organisms have stimulate the development of better methods and techniques.

Another difficult to study UVLPC is that there are not a standard procedure and usually the scientific works describe experiments on different body tissues, that makes very difficult the comparison between the obtained results. In future researches, regulations in relation to this aspect should be established. On the other hand, some authors support the idea that future studies have to be into account the combined effect of different UVLPC, due to their different toxicity and chemical features.

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6. Annex

6.1. Abbreviation list

3-BC: 3-Benzylidene camphor

4-DHB: 4,4'-Dihydroxybenzophenone

4-HB: 4-Hydroxybenzophenone / p-Benzoylphenol

4-MBC: 4-Methylbenzylidene camphor

BP: Benzophenone type

BP-1: (2,4-dihydroxyphenyl) (phenyl)methanone / Benzophenone-1

BP-2: 2,2',4,4'-Tetrahydroxybenzophenone/ Benzophenone-2

BP-3: 2-Hydroxy-4-Methoxybenzophenone / Benzophenone-3 / Oxybenzone

BP-4: 5-Benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid / Benzophenone-4

BP-8: 2,2'-Dihydroxy-4-Methoxybenzophenone / Benzophenone-8/ Dioxybenzone

BS: Benzyl 2-hydroxybenzoate / Benzyl salicylate

BUVs: Benzotriazole UV stabilizers

BZT: 1-H-benzotriazole

d.w.: Dry weight

EHMC: 2-Ethylhexyl 4-methoxycinnamate / Octinoxate

EHS: 2-Ethylhexyl Salicylate / Octisalate

Et-PABA: Ethyl 4-aminobenzoate

HMS: 3,3,5-Trimethylcyclohexyl Salicytale / Homosalate

IMC: Isoamyl 4-methoxycinnamate 3-methylbutyl (E)-3-(4-methoxypenyl)prop-2-enoate / Amiloxate

K_{ow}: Octanol-water partition coefficient

OC: 2-Ethylhexyl 2-cyano-3,3-diphenylacrylate / Octocrylene

OD-PABA: 2-Ethylhexyl 4-(dimethylamino)benzoate

OMC: 2-Ethylhexyl 4-methoxycinnamate / Octinoxate

PABA: 4-aminobenzoate

PCP: Personal care products

PS: Phenyl 2-Hydroxybenzoate / Phenyl salicylate

THB: 2,3,4-Trihydroxybenzophenone / Gallobenzophenone

TiO_2: Titanium Dioxide

UV: Ultraviolet

UV-234: 2-(2H-Benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) phenol

UV-320: 2-(2'-Hydroxy-3',5'-Di-Tert-Butylphenyl) Benzotriazole

UV-326: 2-tert-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol / Bumetrizole

UV-327: 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol

UV-328: 2-(2H-Benzotriazol-2-yl)-4,6-ditertpentylphenol

UV-329: 2-(benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl) phenol / Octrizole

UV-360: 2,2-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol] / Bisoctrizole

UV-571: 2-(2H-Benzotriazol-2-yl)-6-dodecyl-4-methylphenol

UV-9: 2-(2H-Benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol

UV-P: 2-(benzotriazol-2-yl)-4-methylphenol / Drometrizole

VTG: Vitellogenin

ZnO: Zinc Oxide

Valoración Personal Trabajo Fin de Máster

Actividades desarrolladas durante la realización del TFM

- Recopilación de bibliografía relacionada con el tema a tratar
- Lectura bibliográfica
- Realización de un esquema sobre la estructura que llevara el trabajo
- Escritura del trabajo
- Corrección y evaluación sobre el trabajo realizado con ayuda de los tutores asignados

Formación recibida

Al ser un trabajo bibliográfico no se requirió de conocimientos previos sobre ningún programa informático ni cursos.

Nivel de integración e implicación dentro del departamento y relaciones con el personal

Debido a las medidas especiales de aislamiento a causa del Covid-19, el trabajo se realizó enteramente online y no se requirió de asistencia al departamento.

Aspectos positivos y negativos significativos relacionados con el desarrollo del TFM

En cuanto a aspectos positivos he de destacar el poder obtener conocimiento de un área que actualmente es de interés y en el cual se está poniendo cada vez más atención.

Por desgracia, es un TFM que he tenido que realizar de manera enteramente bibliográfica por el tema del covid-19, cuando mi intención es que fuera puramente un TFM experimental. También creo que se debería impartir una clase sobre cómo realizar los diferentes tipos de TFM, ya que siento que hay muchos aspectos que se dan por sentado que ya sabemos y que no son ciertos.

Valoración del aprendizaje conseguido a lo largo del TFM

Al ser la primera vez que me enfrentaba a un trabajo puramente bibliográfico me costó mucho desde el principio poder realizarlo, pero eso también me ayudo a aprender mucho sobre el tema en cuestión a tratar y sobre el trabajo que conlleva realizar un overview. Personalmente, es un tema que me interesó mucho desde el principio y que siento que debería darse más a conocer, ya que desconocía todos estos efectos que pueden tener estos compuestos que utilizamos en la vida cotidiana.