

ARE SUNSCREENS A NEW ENVIRONMENTAL RISK ASSOCIATED TO COASTAL TOURISM?

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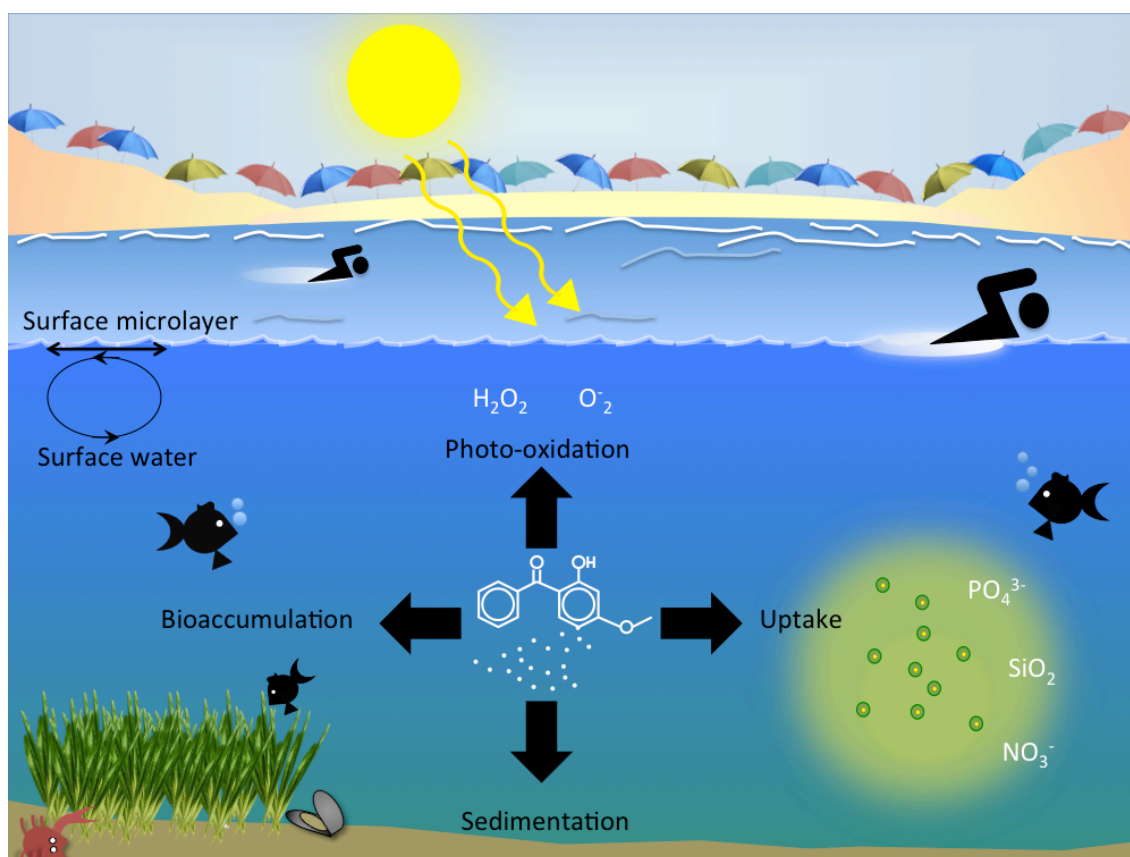
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Abstract

The world coastal-zone population and the coastal tourism are expected to grow during this century. Associated to that, there is an increase in the use of sunscreens, and cosmetics with UV-filters in their formulation, that point out coastal regions worldwide susceptible to receive the impact of these cosmetics. Recent investigations indicate that organic UV-filters and inorganic oxide nanoparticles as well as many other components that are constituents of the sunscreens reach the marine environment and cause harmful effects. This review examines the research studies done on sunscreens in the environment, highlights the environmental risk in coastal areas and suggests future directions.



Keywords: Sunscreens; UV-filters; nanoparticles; coastal tourism; environmental risk; marine pollution.

Highlight:

1. Revision of research studies on sunscreens in the environment.
2. Environmental implications of sunscreen's components into the coastal ecosystem.
3. More studies about sunscreens in the environment need to be addressed.

1 **1. Introduction**

2 Throughout the history of human beings, the sun has been an object of adoration
3 and exploration. However, it was not only an admiration. Since humans lost their pelage
4 and exposed their skin to sunlight they felt the need to protect themselves, either
5 wearing appropriated clothes or by using paints or powders. As far as we know, the
6 ancients Egyptians were the first to use a kind of sunscreen made by olive oil, and this
7 was also the case in Greece and Rome. However, it was at the end of the nineteenth
8 century when it was reported the first scientific research of a sunscreen protection. From
9 1887 to 1934 several compounds that can be used as filters of the ultraviolet radiation
10 (UV-filters) were discovered and in 1928 the first sunscreen was commercially
11 available. It was during these years when international cosmetic companies were born
12 (e.g. L’Oreal, Delial, Piz Buin, Coppertone, etc.) and when sunscreens became widely
13 used among population (Rik Roelandts, 2008; Urbach, 2001). After the World War II, a
14 tanned skin became synonymous of good health and beauty.

15 Nowadays, sunscreens have been shown to give the most effective protection
16 against ultraviolet (UV) radiation damage (Diffey, 2005). A white pale skin has
17 become to be stylish again because people are concerned about skin damage caused by
18 excessive sunlight exposure and thus they have become to use sunscreens all around the
19 globe (Urbach, 2001). Short exposure (between 5 and 10 minutes) to UV radiation has
20 therapeutic effects, i.e. it improves the production of vitamin D and this will increase
21 the calcium absorption, therefore it will prevent from rickets in children and
22 osteoporosis in adults. However, longer exposures can cause severe harm to skin such
23 as skin aging, the erythema (sunburn) and/or melanoma (Holick, 2004).

24 Three segments compose the sun care market: sun protection, after sun and self-
25 tanning. This market increase every year worldwide due to the awareness of the risk
26 associated with the sun exposure (“What’s Hot around the Globe: Insights on Personal
27 Care Products. Global Service Studies Website,;” 2007). Cosmetic companies flood the
28 market every year with new products, formulations and terms like “nanoparticles”,
29 “waterproof” or “broad spectrum” that generates confusion among the user, that are
30 claiming for an effective sunscreen (Kamerow, 2014).

31 Coastal and marine tourism is the fastest growing sector of the global tourism
32 industry. The growth of this sector includes the development of the infrastructures

33 (hotels, ports, second homes, marinas, etc.), water activities and sports (i.e. recreational
34 fishing, yachting, diving, etc.) necessary to accommodate and entertain the large
35 number of visitors to the coastal areas. The impact caused by these activities in the
36 coastal environment has been reported in several studies (Davenport and Davenport,
37 2006; Gormsen, 1997; Hall, 2001). Thus, environmental degradation and pollution (e.g.
38 by yachts fuel, littering, temporally increase of terrestrial runoff, etc.), destruction of
39 habitats (e.g. destruction of coral reefs due to excessive visitations, disturbance of
40 nearshore aquatic life, etc.) or damage to sand-dune ecosystems (e.g. lost of sandy
41 beaches due to onshore construction) are some of the impacts of coastal tourism.

42 Despite that coastal tourism is the fastest growing sector in the world (with the
43 consequent increasing in the use of sunscreen), the implications of sunscreens as a
44 source of new chemicals into the coastal marine system have been poorly evaluated.

45

46 **1.1 Main components of sunscreens**

47 Sunscreen cosmetic could be defined as: “any cosmetic product containing UV-
48 filters in its formulation in order to protect the skin from the solar deleterious UV-light,
49 avoiding or minimizing the damage that this radiation might cause on human health”
50 (Salvador and Chisvert, 2005). Therefore, the most important components of the
51 sunscreens are the UV-filters: substances with range of light absorption in the range of
52 UVA (400 – 320 nm) and/or UVB (320 – 280 nm) and with nearly null absorption of
53 visible radiation (Díaz-Cruz and Barceló, 2009).

54 Concentration limits that can be used in sunscreen formulations depend on the
55 different regulations worldwide (Table 1). UV-filters can be organic (classified into
56 different families: i.e. benzophenone derivatives, salicylates, cinnamates, camphor
57 derivatives, p-aminobenzoic acid and its derivatives, etc. (Chisvert and Salvador,
58 2007)), or inorganic (with only two allowed compounds: titanium dioxide (TiO₂) and
59 zinc oxide (ZnO)). General usage of these inorganic components in the formulation of
60 sunscreens is in the form of nanoparticles (nano-TiO₂ and nano-ZnO, with size around
61 ≤100 nanometers) because they give an effective protection and they do not whiten the
62 skin (Osterwalder et al., 2014). Because its photocatalytic properties, TiO₂ nanoparticles
63 used in sunscreens are coated with aluminum oxide or silica to prevent the formation of

64 reactive oxygen species (ROS) (Jansen et al., 2013a). Commonly, ZnO in sunscreens
65 are in the form of nanorods while TiO₂ are nanoparticles in the rutile structure (Lewicka
66 et al., 2011). L’Oreal Group was the first company that in August 1993 patented the use
67 of nanoparticles of metal oxides as ingredients in sunscreens (Forestier et al., 1995).
68 The action mode of both types of UV-filters are different: while the organic absorbs a
69 specific wavelength, the inorganic ones can give a boarder spectrum protection due to
70 their triple action mode: reflection, scattering and absorption of the UV radiation
71 (Manaia et al., 2013). Normal sunscreens are formed by one or more of these UV-
72 filters: organic, inorganic or a mixture of both. This combination increases the
73 protection giving broad-spectrum sunscreens.

74 Emollients and emulsifiers are present in an elevated percentage in the
75 composition of sunscreens. Emollients play a triple role in the sunscreens composition:
76 they enable solubilization of some UV-filters (i.e. benzoate esters), photostabilization of
77 unstable UV-filters (i.e. butyloctyl salicylates) and they enhance sensorial feeling in
78 terms of spreading, greasiness, stickiness, etc. (i.e. dicaprylyl carbonate) (Osterwalder et
79 al., 2014). Some emollients can also have an inherent UV absorption that increase the
80 broad spectrum of protection. Emulsifiers are amphiphilic molecules that reduce
81 interfacial tension between two immiscible liquids playing an important role in the
82 stability of the emulsion, consistency, skin feel and care properties of the formulation
83 (Al-Bawab and Friberg, 2006; Plass et al., 2001). The emulsifier system defines the
84 emulsion type: traditionally, oil-in-water (O/W) or water-in-oil (W/O) system
85 (Osterwalder et al., 2014), besides new formulations of sunscreens became popular
86 among consumers: oils, water-based and hydroalcoholic lotions and microemulsions,
87 also called easy-to-use sunscreens (Chisvert and Salvador, 2007). Anionic emulsifiers
88 such as alkyl phosphates (i.e. potassium cetyl phosphate) are commonly used to
89 stabilize O/W emulsions and allow the incorporation of inorganic UV-filters (Miller et
90 al., 1999; Osterwalder et al., 2014). Other emulsifiers such as PEG-30
91 dipolyhydroxysterate, stabilized W/O systems improving the water resistance of the
92 sunscreens and they may incorporate lipophilic-coated inorganic UV-filters.

93 In sunscreen composition we can find many other ingredients such as rheology
94 modifiers (thickeners as glycerin or fatty acids), film former agents as acrylates
95 copolymer or silicones, sensory enhancers that improve the skin feeling (i.e. silica,
96 nylon-based compounds, etc.) and in some cases antioxidants such as vitamin C and

97 vitamin E, which are included to reduce the oxidative stress generated by ROS
 98 formation via UV radiation. Moreover, other photoprotective agents in sunscreens
 99 provide protection from erythema and also reduce inflammation and oxidative damage;
 100 as for example carotenoids, polyphenols, algae extracts, nicotiamide (amide form of
 101 vitamin B₃), vitamin A (incorporated as retinyl palmitate), selenium (in the forms of
 102 selenium sulfide or L-selenomethionine, that increase the minimal erythema dose), etc.
 103 (Chen et al., 2012; Chen and Wang, 2012; Jansen et al., 2013b; Osterwalder et al.,
 104 2014).

Table 1. Permitted UV-filters according to the different regulations (Source: “Clinical Guide to Sunscreens and Photoprotection”, edited by Henry W. Lim and Zoe Diana Draeos; Informa Healthcare USA, Inc.).

UV-filter (INCI name)	Maximum concentration (%)										
	USA	EU	Canada	Australia and NZ	China	India	Japan	Korea	South Africa	ASEAN	MERCOSUR
3-Benzylidene camphor		2			2	2			2	2	2
4-Methylbenzylidene camphor		4	6	4	4	4		5		4	4
Benzophenone-1							10		10		
Benzophenone-2							10		10		
Benzophenone-3	6	10	6	10	10	10	5	5	10	10	10
Benzophenone-4	10		6	10	5	5	10	5	5	10 (#)	10
Benzophenone-5		5	6	10	5	5	10		5	5	5
Benzophenone-6							10		10		
Benzophenone-8	3		3	3				3	3	3 (#)	3
Benzophenone-9							10		No limit		
Benzylidene camphor sulfonic acid		6		6	6	6			6	6	6
Bis-ethylhexyloxyphenol methoxyphenyl triazine		10		10	10	10		10	10	10	10
Butyl methoxydibenzoylmethane	3	5		5	5	5	10	5	5	5	5
Camphor benzalkonium methosulfate		6		6 (NZ = 8)	6	6			6	6	6
Cinoxate	3		3	6 (NZ = 3)			5	5	5	3	3
DEA methoxycinnamate			10						8	10	
Diethylamino hydroxy benzoyl hexyl benzoate		10			10						10
Diethylhexyl butamido triazone		10			10	10		10	10	10	10
Digalloyl trioleate								5	5	5 (#)	
Diiisopropyl methylcinnamate							10		10		
Dimethoxyphenyl-[1-(3,4)]-4,4-dimethyl 1,3 pentanedione*							7		7		
Disodium phenyl dibenzylimidazole tetrasulfonate		10		10	10	10		10		10	10
Drometrizole								7			
Drometrizole trisiloxane		15	15	15	15	15	15	15		15	15
Ethyl dihydroxypropyl PABA									5	5	
ethylhexyl dimethoxy benzylidene dioxoimidazole propionate							3				
Ferulic acid*							10		10		

Glyceril octanoate dimethoxycinnamate							10		10		
Glyceril PABA								3	5	3 (#)	
Homosalate	15	10	15	15	10	10	10	10	10	10	15
Isoamyl p-methoxycinnamate		10		10	10	10		10	10	10	10
Isopentyl trimethoxycinnamate trisiloxane*							7.5				
isopropyl methoxycinnamate							10		10		
isopropyl salicylate*									4		
menthyl anthranilate	5		5	5				5	5	5 (#)	5
Methylene bis-benzotriazolyl tetramethylbutylphenol		10		10	10	10	10			10	10
Octocrylene	10	10	12	10	10	10	10	10		10	10
Octyl dimethyl PABA	8	8	8	8	8	8	10	8	8	8	8
Octyl methoxycinnamate	7.5	10	8.5	10	10	10	20	7.5	10	10	10
Octyl salicylate	5	5	6	5	5	5	10	5	5	5	5
Octyl triazone		5		5	5	5	3	5	5	5	5
PABA	15	5	5	15	5	5	4	5		5	15
PEG-25 PABA		10		10	10	10				10	10
Pentyl dimethyl PABA*							10			5	
Phenylbenzimidazole sulfonic acid	4	8	8	4	8	8	3	4		8	8
Polyacrylamidomethyl benzylidene camphor		6			6	6				6	6
Polysilicone-15		10		10	10		10	10	10	10	10
TEA salicylate	12		12	12						12	12
Terephthalylidene dicamphor sulfonic acid		10	10	10	10	10	10	10		10	10
Titanium dioxide	25	25	25	25	25		No limit	25		25	25
Zinc oxide	25		25	No limit (NZ = 25)	25		No limit	25		20	25
β, 2-glucopyranoxy propyl hydroxy benzophenone*							5		5		

INCI: International Nomenclature of Cosmetic Ingredients; (*) no INCI name; NZ: New Zealand; (#) Permitted only in Thailand; ASEAN (Brunei, Cambodia, Indonesia, Laos, Malaysia, Myanmar, Philippines, Singapore, Thailand and Vietnam); MERCOSUR (Argentina, Brazil, Paraguay and Uruguay).
Reference: (Farah K. Ahmed, 2008).

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106 2. Analytical methodologies for the determination of UV-filters in environmental 107 samples

108 Although the development of sensitive analytical methodologies during last
109 years has allowed the determination of UV-filters and its derivatives in different
110 environmental compartments, information about the presence and concentrations of
111 these components in the marine environment is very scarce.

112 2.1 Organic UV-filters

113 There are 50 organic compounds allowed by different legislations to be used as

114 UV-filters in sunscreen composition (Table 1). However, only 16 have been analyzed in
 115 environmental matrices (Table 2), therefore the environmental implications of organic
 116 UV-filters cannot be completely estimated.

Table 2. Organic UV-filters studied in environmental matrices.

	INCI name ^a	CAS N°	Empirical formula
3-BC	3-Benzylidene camphor	15087-24-8	C ₁₇ H ₂₀ O
4-MBC	4-Methylbenzylidene camphor	36861-47-9	C ₁₈ H ₂₂ O
BDM	Butyl methoxydibenzoylmethane	70356-09-1	C ₂₀ H ₂₂ O ₃
BZ-1	Benzophenone-1	131-56-6	C ₁₃ H ₁₀ O ₃
BZ-2	Benzophenone-2	131-55-5	C ₁₃ H ₁₀ O ₅
BZ-3	Benzophenone-3	131-57-7	C ₁₄ H ₁₂ O ₃
BZ-4	Benzophenone-4	4065-45-6	C ₁₄ H ₁₂ O ₆ S
BZ-8	Benzophenone-8	131-53-3	C ₁₄ H ₁₂ O ₄
HS	Homosalate	118-56-9	C ₁₆ H ₂₂ O ₃
IMC	isoamyl p-methoxycinnamate	71617-10-2	C ₁₅ H ₂₀ O ₃
OCR	Octocrylene	6197-30-4	C ₂₄ H ₂₇ NO ₂
ODP	Octyl dimethyl PABA	21245-02-3	C ₁₇ H ₂₇ NO ₂
OMC	Octyl methoxycinnamate	5466-77-3	C ₁₈ H ₂₆ O ₃
OS	Octyl salicylate	118-60-5	C ₁₅ H ₂₂ O ₃
OT	Octyl triazone	88122-99-0	C ₄₈ H ₆₆ N ₆ O ₆
PBS	Phenylbenzimidazole sulphonic acid	27503-81-7	C ₁₃ H ₁₀ N ₂ O ₃ S

^a INCI (International Nomenclature for Cosmetic Ingredients) elaborated by the Personal Care Products Council (CTFA) and the European cosmetic, toiletry and perfumery industry (COLIPA). CAS N° (numerical identifier assigned by Chemical Abstracts Service).

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118 Many analytical methodologies have been developed for the determination of
 119 organic UV-filters in different natural matrices (Díaz-Cruz and Barceló, 2009; Salvador
 120 and Chisvert, 2005). Due to the very low concentration of organic UV-filters in the
 121 environment (ranging from pM to nM), a pre-concentration step is necessary previous to
 122 the analysis (mostly based on extraction and microextraction procedures such as

123 pressurized liquid extraction, ionic liquid-based single drop microextraction, stir bar
124 sorptive extraction, dispersive liquid-liquid microextraction, solid-phase extraction and
125 microextraction, micelle mediated extraction-solvent back extraction, non-porous
126 membrane-assisted liquid-liquid extraction, etc.). Pre-concentrated analytes are usually
127 separated and quantified by chromatographic techniques coupled with mass
128 spectrometry detection (LC-MS/MS, GC-MS/MS, UHPLC-MS/MS, etc.) (Benedé et
129 al., 2014a, 2014b; Bratkovics and Sapozhnikova, 2011; Cuderman and Heath, 2007;
130 Gago-Ferrero et al., 2013b, 2013c, 2011a; Giokas et al., 2005, 2004; Gómez et al.,
131 2009; Lambropoulou et al., 2002; Magi et al., 2012; Nguyen et al., 2011; Oliveira et al.,
132 2010; Pedrouzo et al., 2010, 2009; Rodil et al., 2009a, 2009b, 2009c; Rodil and Moeder,
133 2008; Sánchez-Brunete et al., 2011; Tarazona et al., 2010; Trenholm et al., 2008; Vidal
134 et al., 2010; Wick et al., 2010). Passive sampling devices are sometimes used to
135 sampling during large periods of time. For example, the use of semipermeable
136 membrane devices (SPMDs) were used in Swiss lakes and rivers during 3 weeks
137 (Balmer et al., 2005; Buser et al., 2005) and during a cruiser across the Pacific Ocean
138 (Goksøyr et al., 2009).

139 **2.2 Inorganic UV-filters**

140 Some analytical approaches have also been proposed for the determination of
141 titanium dioxide nanoparticles as the main inorganic UV-filters in the marine
142 environment. Analytical methodologies for the analysis of nanoparticles in
143 environmental matrices imply separation methods (e.g. size-exclusion chromatography,
144 hydrodynamic chromatography, counter-current chromatography, electrophoresis and
145 capillary electrophoresis or field-flow fractionation), electron microscopy techniques
146 (e.g. transmission electron microscopy, scanning electron microscopy, scanning tunnel
147 microscopy and atomic force microscopy), scattering (dynamic light scattering) and
148 spectroscopy techniques (nuclear magnetic resonance and X-ray spectroscopy) (Farré
149 and Barceló, 2012; López-Heras et al., 2014). In addition to the composition, these
150 techniques provide information about concentration, size distribution, crystallographic
151 structure and morphology. Because of the lack of accuracy methodologies for the
152 analysis of nanomaterials in the complex matrix of seawater, concentration of total Ti^{4+}
153 after acid digestion is often reported (Luo et al., 2014). In that sense, recently it has
154 been reported a new procedure for the determination of Ti^{4+} in environmental samples
155 (Sánchez-Quiles et al., 2013).

156 Analysis of nanoparticles in marine environmental samples is limited due to the
157 lack of reliable methods for its detection and quantification. In addition to the electronic
158 microscopy and particle size techniques (such as hydrodynamic chromatography or
159 electrophoresis), news methods based on asymmetrical flow field-flow fractionation
160 coupled to ICP-MS (asFIFFF-ICP-MS) and single particle ICP-MS (SP-ICP-MS) have
161 been reported for analysis of nano-TiO₂ in different environmental samples (Laborda et
162 al., 2014; Lee et al., 2014; López-Heras et al., 2014). Although these methods have
163 demonstrated to be useful for analysis of nanoparticles they have not been tested in
164 seawater samples.

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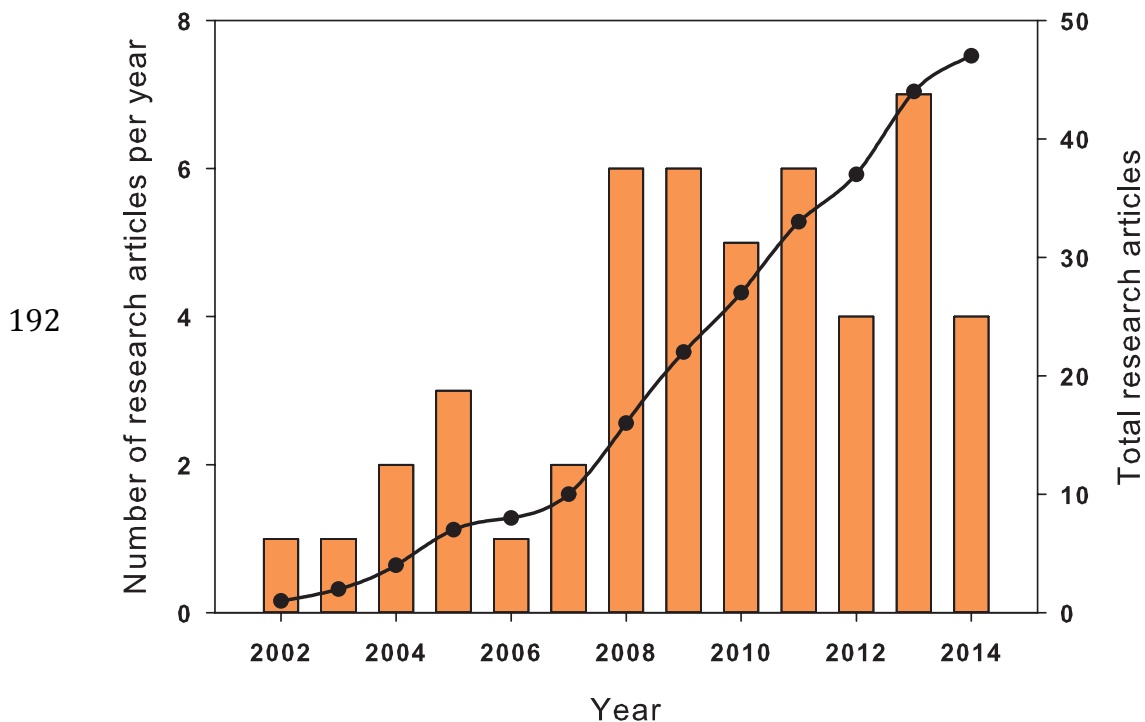
166 **3. Sunscreens in the environment**

167 In parallel with the development of new analytical methodologies,
168 ecotoxicological assays have been performed in aquatic organisms in order to establish
169 the toxicity thresholds for these compounds.

170 It is expected that, on the skin, UV-filters should be photostable under sunlight,
171 however in aqueous media can undergo to a undesirable products that could
172 compromise their UV absorption properties (Santos et al., 2012). Organic UV-filters
173 can undergo to degradation products by different mechanisms: photolysis and
174 photoisomerization, break down by products in wastewater treatment plants (WWTP) or
175 can be metabolized by kidneys after topical application and their metabolites can be
176 excreted in the urine (Díaz-Cruz et al., 2008). UV-filters can reach the marine
177 environment mainly by two different ways: directly as consequence of water
178 recreational activities and indirectly from WWTP effluents (Díaz-Cruz and Barceló,
179 2009; Giokas et al., 2007).

180 As a consequence of the increasing coastal tourism and the use of sunscreens the
181 interest of researchers in the determination of organic UV-filters in different
182 environmental and urban compartments has increased in last years (Figure 1). Because
183 WWTP cannot remove efficiently high concentrations of the organic UV-filters, and in
184 spite of the natural degradation that occurs in the environment, these compounds are
185 present in effluents and freshwaters that finally can reach to the sea. Sunscreen organic
186 components have been determined in seawater, freshwaters (rivers and lakes),

187 sediments, WWTP influents and effluents, swimming pools, urban groundwater and
188 even in tap water (Table 3). These ingredients even have been found in the lipid tissue
189 of natural populations of aquatic organisms such as mussels, crustacean, eels, fishes,
190 marine mammals and aquatic birds (Table 3), suggesting that bioaccumulation of
191 organic UV-filters in the food webs may be happening.



193 Figure 1: Published research articles reporting environmental concentrations of organic
194 UV-filters. Bars represent research articles each year and black line represents the total
195 accumulated articles.

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Table 3. Sample, analytical methodologies, detection limits and range of concentrations of the organic UV-filters in environmental samples.

Organic UV-filter	Sample	Concentration
3-BC	Seawater*	9 – 13 ng L ⁻¹
4-MBC	Seawater*	n.d. - 798.7 ng L ⁻¹
	River water	n.d. - 140 ng L ⁻¹
	Lake water	n.d. - 1,140 ± 50 ng L ⁻¹
	WWTP (Influent)	n.d. - 2.7 µg L ⁻¹
	WWTP (Effluent)	n.d. - 6.5 µg L ⁻¹
	Swimming pool	n.d. - 330 ng L ⁻¹
	Tap water	n.d. - 18 ng L ⁻¹
	Urban groundwater	n.d. - 13.9 ng L ⁻¹
	Marine sediments	n.d. - 7.90 ng g ⁻¹ d.w.
	River sediments	n.d. - 17.2 ng g ⁻¹ d.w.
	Lake sediments	n.d.
	STP effluent sediments	n.d.
	Beach sand	n.d. - 2.0 ± 0.4 ng g ⁻¹ d.w.
	Sewage sludge	150 – 4,980 ng g ⁻¹ d.w.
	<i>Coregonus sp.</i>	n.d.
	<i>Rutilus rutilus</i>	44 - 94 ng g ⁻¹ lipid
	<i>Perca fluviatilis</i>	166 ng g ⁻¹ lipid
	<i>Luciobarbus sclareti</i>	n.d.
	<i>Cyprinus carpio</i>	n.d.
	<i>Leuciscus cephalus/Barbus barbus</i>	n.d.
BDM	Seawater	n.d. - 321 ng L ⁻¹
	Lake water	< 20 - 2,431 ± 22 ng L ⁻¹
	WWTP (Influent)	35.0 - 1,290.2 ng L ⁻¹
	WWTP (Effluent)	n.d. - 1,018.3 ng L ⁻¹
	Swimming pool	n.d.
	Sewage sludge	517 ± 78 ng g ⁻¹ d.w.
BZ-1	Seawater	n.d. - 280 ± 30 ng L ⁻¹
	River water	< 0.3 - 17 ng L ⁻¹
	WWTP (Influent)	n.d. - 722 ng L ⁻¹
	WWTP (Effluent)	n.d. - 155.0 ng L ⁻¹
	Urban groundwater	n.d. - 19.4 ng L ⁻¹
	Marine sediments	n.d.
	River sediments	n.d.
	Agricultural soil	n.d.
	Industrial soil	n.d. - 5.7 ± 0.3 ng g ⁻¹
	Activated sludges	5.1 ± 1.5 ng gTSS ⁻¹
	Sewage sludge	n.d.
	<i>Luciobarbus sclareti</i>	n.d.
	<i>Cyprinus carpio</i>	n.d.
BZ-2	River water	n.d. - 284 ng L ⁻¹
	WWTP (Influent)	n.d. - 93 ± 10 ng L ⁻¹

	WWTP (Effluent)	n.d. - 14 ± 3 ng L ⁻¹
	Urban groundwater	n.d.
	Activated sludges	11 ± 2 ng gTSS ⁻¹
BZ-3	Seawater*	n.d. - 3,300 ± 200 ng L ⁻¹
	River water	n.d. - 114 ng L ⁻¹
	Lake water	< 2 - 125 ng L ⁻¹
	WWTP (Influent)	n.d. - 7.8 µg L ⁻¹
	WWTP (Effluent)	< 0.01 - 0.7 µg L ⁻¹
	Swimming pool	n.d. - 3.3 µg L ⁻¹
	Tap water	n.d.
	Urban groundwater	n.d. - 34 ng L ⁻¹
	Marine sediments	n.d. - 2.96 ng g ⁻¹ d.w.
	River sediments	n.d. - 47 ± 13.1 ng g ⁻¹ d.w.
	Lake sediments	n.d.
	Beach sand	n.d. - 1.0 ± 0.1 ng g ⁻¹ d.w.
	Agricultural soil	n.d.
	Industrial soil	n.d.
	STP effluent sediments	n.d.
	Activated sludges	132 ± 23 ng gTSS ⁻¹
	Sewage sludge	n.d. - 0.79 µg g ⁻¹ d.w.
	<i>Coregonus sp.</i>	n.d.
	<i>Rutilus rutilus</i>	66 - 118 ng g ⁻¹ lipid
	<i>Perca fluviatilis</i>	123 ng g ⁻¹ lipid
	<i>Luciobarbus sclareti</i>	n.d. - 24.3 ng g ⁻¹ d.w.
	<i>Cyprinus carpio</i>	11.2 ng g ⁻¹ d.w.
	<i>Phalacrocorax sp.</i>	n.d.
	<i>Dreissena polymorpha</i>	n.d.
	<i>Gammarus sp.</i>	n.d.
	<i>Leuciscus cephalus</i>	n.d.
	<i>Salmo trutta</i>	n.d. - 151 ng g ⁻¹ lipid
	<i>Barbus barbus</i>	n.d.
	<i>Anguilla anguilla</i>	n.d.
BZ-4	Seawater	< 1 ng L ⁻¹
	River water	< 3 - 1,980 ± 130 ng L ⁻¹
	WWTP (Influent)	n.d. - 4,858 ± 1,101 ng L ⁻¹
	WWTP (Effluent)	n.d. - 1,947 ± 34 ng L ⁻¹
	Tap water	n.d. - 18 ng L ⁻¹
	Urban groundwater	n.d. - 36.6 ng L ⁻¹
	Activated sludges	29 ± 7 ng gTSS ⁻¹
	<i>Leuciscus cephalus/Barbus barbus</i>	n.d.
BZ-6	Marine sediments	n.d.
	River sediments	n.d. - 6.1 ± 0.3 ng g ⁻¹
	Agricultural soil	n.d. - 0.6 ± 0.4 ng g ⁻¹
	Industrial soil	n.d.
BZ-8	Seawater	n.d.
	River water	n.d.

	WWTP (Influent)	n.d. - 185 ng L ⁻¹
	WWTP (Effluent)	n.d. - 83.5 ng L ⁻¹
	Urban groundwater	n.d.
	Marine sediments	n.d.
	River sediments	n.d.
	Agricultural soil	n.d.
	Industrial soil	n.d.
HS	Seawater	n.d. - 310 ± 20 ng L ⁻¹
	River water	n.d. - 345 ng L ⁻¹
	Lake water	n.d.
	WWTP (Influent)	n.d. - 1,650.4 ng L ⁻¹
	WWTP (Effluent)	n.d. - 154.2 ng L ⁻¹
	Swimming pool	n.d.
	Marine sediments	n.d.
	River sediments	n.d. - 26 µg kg ⁻¹ d.w.
	Lake sediments	n.d.
	Beach sand	n.d. - 4.9 ± 0.7 ng g ⁻¹ d.w.
	Agricultural soil	n.d.
	Industrial soil	n.d.
	STP effluent	n.d.
	Sewage sludge	331 ± 47 ng g ⁻¹ d.w.
IMC	Seawater	n.d. - 280 ± 20 ng L ⁻¹
	River water	n.d.
	Lake water	146 ± 20 ng L ⁻¹
	WWTP (Influent)	n.d. - 226.0 ng L ⁻¹
	WWTP (Effluent)	n.d. - 165.5 ng L ⁻¹
	Swimming pool	700 ± 300 ng L ⁻¹
	Tap water	n.d.
	Lake sediments	n.d.
	Beach sand	n.d. - 1.3 ± 0.3 ng g ⁻¹ d.w.
	Sewage sludge	20 ± 3 ng g ⁻¹ d.w.
OCR	Seawater	n.d. - 2,780.7 ng L ⁻¹
	River water	n.d. - 283 ng L ⁻¹
	Lake water	n.d. - 4,381 ± 539 ng L ⁻¹
	WWTP (Influent)	n.d. - 5,322 ± 612 ng L ⁻¹
	WWTP (Effluent)	n.d. - 0.2 ± 0.06 µg L ⁻¹
	Run off water	3 ng L ⁻¹
	Swimming pool	n.d. - 15 ng L ⁻¹
	Tap water	n.d.
	River sediments	n.d. - 2,400 ng g ⁻¹ d.w.
	Lake sediments	61 ± 5 - 93 ± 4 ng g ⁻¹
	STP effluent sediments	1.2 µg kg ⁻¹ d.w.
	Sediments	2 - 5 µg kg ⁻¹
	Beach sand	1.7 ± 0.4 - 25 ± 3 ng g ⁻¹ d.w.
Sewage sludge	320 - 18,740 ng g ⁻¹ d.w.	
<i>Coregonus sp.</i>	n.d.	

	<i>Rutilus rutilus</i>	n.d.	
	<i>Perca fluviatilis</i>	25 ng g ⁻¹ lipid	
	<i>Pontoporia blainvillei</i>	n.d. - 712 ng g ⁻¹ lipid	
	<i>Mytilus Sp.</i>	n.d. - 7,112 ng g ⁻¹ d.w.	
	<i>Luciobarbus sclareti</i>	n.d. - 30.4 ng g ⁻¹ d.w.	
	<i>Cyprinus carpio</i>	n.d.	
ODP	Seawater	n.d. - 390 ± 40 ng L ⁻¹	
	River water	n.d. - 47 ng L ⁻¹	
	Lake water	n.d. - 34 ng L ⁻¹	
	WWTP (Influent)	n.d. - 376.9 ng L ⁻¹	
	WWTP (Effluent)	n.d. - 224.3 ng L ⁻¹	
	Swimming pool	n.d. - 2.1 µg L ⁻¹	
	Tap water	n.d. - 2.3 ng L ⁻¹	
	Urban groundwater	n.d.	
	River sediments	n.d. - 17 ± 3 ng g ⁻¹ d.w.	
	Lake sediments	n.d.	
	STP effluent sediments	n.d.	
	Beach sand	n.d.	
	Sewage sludge	1.9 ± 0.3 ng g ⁻¹ d.w.	
	<i>Luciobarbus sclareti</i>	n.d.	
	<i>Cyprinus carpio</i>	n.d.	
	OMC	Seawater*	n.d. - 389.9 ng L ⁻¹
		River water	n.d. - 153 ng L ⁻¹
Lake water		n.d. - 3,009 ± 206 ng L ⁻¹	
WWTP (Influent)		n.d. - 1.9 µg L ⁻¹	
WWTP (Effluent)		n.d. - 505.2 ng L ⁻¹	
Run off water		n.d.	
Swimming pool		n.d. - 86 ± 7 ng L ⁻¹	
Tap water		n.d.	
Marine sediments		n.d. - 17.8 ng g ⁻¹ d.w.	
River sediments		n.d. - 101 µg kg ⁻¹ d.w.	
Lake sediments		14 ± 4 - 34 ± 6 ng g ⁻¹	
STP effluent sediments		14 µg kg ⁻¹ d.w.	
Sediments		34 - 880 µg kg ⁻¹	
Beach sand		n.d. - 10 ± 1 ng g ⁻¹ d.w.	
Sewage sludge		n.d. - 3.35 µg g ⁻¹ d.w.	
<i>Coregonus sp.</i>		n.d. - 72 ng g ⁻¹ lipid	
<i>Rutilus rutilus</i>		n.d. - 64 ng g ⁻¹ lipid	
<i>Perca fluviatilis</i>		n.d.	
<i>Mytilus Sp.</i>		3 - 256 ng g ⁻¹ d.w.	
<i>Luciobarbus sclareti</i>		n.d. - 241.7 ng g ⁻¹ d.w.	
<i>Cyprinus carpio</i>		n.d.	
<i>Phalacrocorax sp.</i>		16 - 701 ng g ⁻¹ lipid	
<i>Dreissena polymorpha</i>		22 - 150 ng g ⁻¹ lipid	
<i>Gammarus sp.</i>	91 - 133 ng g ⁻¹ lipid		
<i>Leuciscus cephalus</i>	23 - 79 ng g ⁻¹ lipid		

	<i>Salmo trutta</i>	n.d. – 205 ng g ⁻¹ lipid
	<i>Barbus barbus</i>	n.d. – 337 ng g ⁻¹ lipid
	<i>Anguilla anguilla</i>	30 ng g ⁻¹ lipid
	<i>Leuciscus cephalus/Barbus barbus</i>	4 ± 5 – 142 ± 95 ng g ⁻¹ lipid
OS	Seawater	n.d. - 880 ± 30 ng L ⁻¹
	River water	n.d. - 266 ng L ⁻¹
	Lake water	748 ± 60 ng L ⁻¹
	WWTP (Influent)	n.d. - 1,188.3 ng L ⁻¹
	WWTP (Effluent)	n.d. - 128.9 ng L ⁻¹
	Swimming pool	n.d.
	Marine sediments	13.3 ± 0.4 ng g ⁻¹
	River sediments	n.d. - 20.0 ± 0.5 ng g ⁻¹
	Lake sediments	n.d.
	Beach sand	1.8 ± 0.5 – 12 ± 1 ng g ⁻¹ d.w.
	Agricultural soil	n.d.
	Industrial soil	n.d.
	STP effluent sediments	n.d.
	Sewage sludge	280 ± 37 ng g ⁻¹ d.w.
OT	Sewage sludge	700 – 27,700 ng g ⁻¹ d.w.
PBS	Seawater	n.d.
	River water	48 ± 3 - 3,240 ± 140 ng L ⁻¹
	WWTP (Influent)	196 ± 56 - 3,890 ± 170 ng L ⁻¹
	WWTP (Effluent)	n.d. - 1,820 ± 240 ng L ⁻¹
	Tap water	n.d.
	Activated sludges	n.d.

* Including surface microlayer; River water (river and stream); n.d. (no detected); d.w. (dry weight); WWTP (waste water treatment plant); STP (sewage treatment plant).

References: (Amine et al., 2012; Arukwe et al., 2012; Bachelot et al., 2012; Balmer et al., 2005; Barón et al., 2013; Benedé et al., 2014b; Bratkovics and Sapozhnikova, 2011; Buser et al., 2005; Cuderman and Heath, 2007; Fent et al., 2010b; Gago-Ferrero et al., 2013a, 2013b, 2013c, 2011a, 2011b; Giokas et al., 2005, 2004; Goksøyr et al., 2009; Gómez et al., 2009; Jurado et al., 2014; Kameda et al., 2011; Kasprzyk-Hordern et al., 2008; Kawaguchi et al., 2008; Lambropoulou et al., 2002; Langford and Thomas, 2008; Li et al., 2007; Magi et al., 2012; Nguyen et al., 2011; Pedrouzo et al., 2010, 2009; Pintado-Herrera et al., 2013; Plagellat et al., 2006; Poiger et al., 2004; Ricking et al., 2003; Rodil et al., 2009a, 2009b, 2009c; Rodil and Moeder, 2008; Sánchez-Brunete et al., 2011; Tarazona et al., 2014, 2010; Tashiro and Kameda, 2013; Tovar-Sánchez et al., 2013; Trenholm et al., 2008; Tsui et al., 2014; Vidal et al., 2010; Wick et al., 2010; Zenker et al., 2008)

203

204 Many ecotoxicological studies have been done to assess the potential damage of
 205 sunscreens and their components. *In vitro* experiments have demonstrated that organic
 206 UV-filters might be toxic for some aquatic microorganism. For example, Sieratowicz et
 207 al. (2011) calculated the half maximal inhibitory concentration (IC₅₀) of benzophenone-
 208 3 (BZ-3), 3-benzylidene camphor (3-BC) and 4-methyl benzylidene camphor (4-MBC)

209 for a freshwater phytoplankton specie *Desmodesmus subspicatus* (0.96 mg L⁻¹, 6.99 mg
210 L⁻¹ and 7.66 mg L⁻¹, respectively) in 72 hours culture experiment. More recently,
211 Paredes et al. (2014) have calculated the toxicity according to the half maximal
212 effective concentration (EC₅₀) in the specie *Isochrysis galbana* concluding that toxicity
213 decreases from BZ-3, octyl methoxycinnamate (OMC), 4- MBC and benzophenone-4
214 (BZ-4) with EC₅₀ of 13.87 ng mL⁻¹, 74.72 ng mL⁻¹, 171,45 ng mL⁻¹ and > 10,000 ng
215 mL⁻¹, respectively. In the protozoan *Tetrahymena thermophila* BZ-3 and 4-MBC could
216 inhibit the growth (EC₅₀ of 7.5 mg L⁻¹ and 5.1 mg L⁻¹, respectively) in 24h of culture
217 experiments (Gao et al., 2013). The ecotoxicity of UV-filters in crustacean *Daphnia*
218 *magna* showed after 48 h that OMC was more toxic than 4-MBC, BZ-3, 3-BC and BZ-4
219 (EC₅₀ of 0.29 - 0.57 mg L⁻¹, 0.56 - 0.80 mg L⁻¹, 1.67 – 1.9 mg L⁻¹, 3.61 mg L⁻¹ and 50
220 mg L⁻¹, respectively) (Fent et al., 2010a; Sieratowicz et al., 2011).

221 Evaluated the toxicity of four UV-filters in marine invertebrates, *Mytilus*
222 *galloprovincialis* (mussels), *Paracentrotus lividus* (sea urchins) and *Siriella armata*
223 (crustacea), the following conclusion has been reached: OMC and 4-MBC were the
224 most toxics, whereas BZ-4 presented the lowest toxicity (Paredes et al., 2014). Also
225 OMC showed toxic effects on snails (*Melanoides tuberculata* and *Potamopyrgus*
226 *antipodarum*) while butyl methoxydibenzoylmethane (BDM) and octocrylene (OCR)
227 showed no effects (Kaiser et al., 2012).

228 Hormonal effects (estrogenic, antiestrogenic, androgenic and antiandrogenic
229 activities) of some organic UV-filters have been extensively studied using *in vitro* test
230 in human cells, fishes and frogs (Díaz-Cruz and Barceló, 2009; Kim and Choi, 2014 and
231 references therein). Different studies carried out in fishes have demonstrated that
232 concentrations of organic UV-filters may induce change in genes in hormonal
233 pathways, for example concentrations in the order of µg L⁻¹ of BZ-3, BZ-4 or OMC
234 down-regulated the expression of genes involved in the sex hormone of *Danio rerio*
235 (zebrafish) at two different life stages, eleuthero-embryos and adult (Blüthgen et al.,
236 2012; Zucchi et al., 2011a, 2011b).

237 Due to its composition, sunscreens are a source of H₂O₂ into the coastal marine
238 waters. It has been demonstrated that under UV radiation some organic UV-filters (e.g.
239 BZ-3, OCR, OMC, PBSA, PABA, etc.) can generate ROS (O₂⁻, OH[·], H₂O₂, etc.) (Allen
240 et al., 1996; Hanson et al., 2006; Inbaraj et al., 2002). Sánchez-Quiles and Tovar-

241 Sánchez (2014) demonstrated that sunscreens may increase the concentration of H₂O₂
242 up to 270 nM/day in a Mediterranean Beach. These oxidizing species can damage
243 lipids, proteins and DNA and they can generate high stress levels in marine organisms
244 (Lesser, 2006, and references therein). But not only these organic UV-filters can
245 generate ROS, other studies point out that inorganic UV-filters (i.e. TiO₂ and ZnO),
246 under UV radiation results toxic for the marine phytoplankton. Many studies agree that
247 the toxicity of nano-TiO₂ is produced by its photochemical properties under solar
248 radiation, that depends on the radiation intensity and the crystalline structure and
249 concentration of the nanoparticles (Hund-Rinke and Simon, 2006; Li et al., 2014;
250 Mansfield et al., 2015). Even though nanoparticles are usually covered with an inert
251 coating layer to avoid its photoreactivity, this layer is dissolved in aquatic environments
252 after being released from sunscreens (Botta et al., 2011; Labille et al., 2010). A recently
253 published review about phototoxicity of nano-TiO₂ calculates the “phototoxicity ratio”
254 obtained with experiments conducted in presence and absence of sunlight and concludes
255 that phototoxicity of nano-TiO₂, under solar radiation, is specially harmful for the order
256 Cladocera (Jovanović, 2015).

257 Very little is known about the worldwide production of these two oxide
258 nanoparticles. In accordance with the United States Environmental Protection Agency
259 (US EPA), in 2005 the global production of nano-TiO₂ was estimated at 2,000 tons and
260 during the period 2006-2010 has been calculated at 5,000 tons per year (US EPA
261 National Center for Environmental Assessment and Powers). However, there are others
262 estimations of this production, thus Piccinno et al. (2012) estimated, based on an
263 industry survey, a global production of 550 to 5,500 tons per year. According to
264 Aschberger et al. (2011) the estimated production is about 60,000 tons per year. The
265 global production of nano-ZnO was calculated also in several studies, thus while
266 Piccinno et al. (2012) calculated a production between 55 and 550 tons per year,
267 Aschberger et al. (2011) estimated in 10,000 tons per year the nano-ZnO production. It
268 is believed that 60 % of nano-TiO₂ and 80 % of nano-ZnO of the global production are
269 used in cosmetic products (Piccinno et al., 2012). These nanoparticles can reach the
270 marine environment during their entire life cycle (i.e. production of nanoparticles,
271 fabrication and use of products) via air deposition, WWTP effluents and/or direct
272 release (Baker et al., 2014; Sun et al., 2014). Once in the seawater they can interact with
273 aquatic organisms in different ways: adsorption to the surface of microorganisms,

274 cellular internalization, trapping by filter feeder organisms (e.g. bivalves), ingest by
275 benthic fauna from the sediments or uptake by fishes (Baker et al., 2014). Sánchez-
276 Quiles and Tovar-Sánchez (2014) estimated that in a touristic beach during a summer
277 day about 4 kg of TiO₂ nanoparticles could be released from sunscreens into seawater.
278 Other authors suggest that recreational activities that take place at the Old Danube Lake
279 may imply a consumption of sunscreen of 8.1 tons per year, and estimated that 94.5 Kg
280 of TiO₂ per year may released in the lake waters (Gondikas et al., 2014).

281 Many studies provide evidence of the toxicity of nanoparticles in aquatic
282 organisms and most of them (64 %) were performed on fresh waters species, and only
283 14 % were on salt water species (Minetto et al., 2014). Miller et al. (2010) demonstrated
284 that nano-ZnO produces inhibition growth in four species of marine phytoplankton with
285 concentrations between 0.5 and 1.0 mg L⁻¹, while nano-TiO₂ does not present any
286 significantly effects at these concentrations. Ma et al. (2012) demonstrated that
287 phototoxicity of nano-TiO₂ increased between 2 to 4 times under simulating solar
288 radiation, being *Daphnia magna* 100 times more sensible than fish Japanese medaka
289 (*Oryzias latipes*). The effects of long-term exposure of cladoceran *Daphnia magna* to
290 nano-TiO₂ were studied over six generations showing that chronic exposure to 1.78 mg
291 L⁻¹ of nano-TiO₂ resulted in 100 % mortality (Jacobasch et al., 2014). A similar study in
292 zebrafish (*Danio rerio*) demonstrated that, after six months of exposure, nano-TiO₂ was
293 bioaccumulated in brain, gill, liver and heart, producing organ injury and mortality
294 (Chen et al., 2011).

295 To our knowledge, few studies address the environmental implications of the
296 totally composition of sunscreens. The first study that provided the toxic effect of
297 sunscreens in the marine environment was carried out by Danovaro and Corinaldesi
298 (2003), who demonstrated that sunscreens induce viral infections and control marine
299 bacterioplankton. The same authors demonstrated that sunscreens affect corals
300 bleachings by promoting the lytic viral cycle, killing the symbiotic microalgae
301 *zooxanthellae* (Danovaro et al., 2008). On the other hand, Tovar-Sánchez et al. (2013)
302 demonstrated, with laboratory experiments and field measurements, that sunscreens are
303 an important source of nutrients (nitrate (NO₃⁻), nitrite (NO₂⁻), phosphate (PO₄³⁻),
304 silicate (SiO₂) and ammonium (NH₄⁺)) to the coastal marine environment that could
305 enhance the primary production in the oligotrophic waters of the Mediterranean Sea.

306 A study carried out on a touristic beach indicates that exist a temporal (daily)
307 and vertical (water column) distribution of UV chemical filters and H₂O₂ concentrations
308 in coastal waters, with the highest concentrations of UV-filters measured in the surface
309 microlayer (SML) (Sánchez-Quiles and Tovar-Sánchez, 2014; Tovar-Sánchez et al.,
310 2013). According to these authors, concentrations of chemicals in the first centimeter of
311 the sea surface water (SML) were up to 41.5 % for BZ-3, 43.0 % for 4-MBC and 41.6
312 % for H₂O₂ higher than in the immediately subsurface waters. Because of its
313 lipophilicity (e.g. log K_{ow} of 3.79 and 4.95 for BZ-3 and 4-MBC, respectively) these
314 compounds tend to accumulate in the SML and in muscle and adipose tissues of marine
315 organisms (Gago-Ferrero et al., 2012), thus elevated concentrations of OCR were found
316 in the liver of Franciscana dolphin (*Pontoporia blainvillei*) from Brazil (up to 712 ng g⁻¹
317 lipid) (Gago-Ferrero et al., 2013a) or in mussels (*Mytilus Sp.*) collected along the
318 French coast (up to 7,112 ng g⁻¹ d.w.) (Bachelot et al., 2012) (Table 3). Goksøyr et al.
319 (2009) reported concentrations of organic UV-filters in open waters of the Pacific,
320 providing evidence of the persistence and wide dispersion of these components in the
321 marine environment.

322 The toxic effects of sunscreens and their main components have opened a debate
323 about the regulation and labeling of sunscreens. In accordance with their chemical
324 composition (Sobek et al., 2013) suggested that sunscreens should be labeled according
325 to the European Union CLP regulation (classification, labeling and packaging; EC
326 1272/2008). Therefore sunscreens with ingredients that could be a risk for marine
327 environment (e.g. nano-TiO₂), should be labeled with hazard statements or even labeled
328 with hazard pictograms, as occurs with other products that include the same
329 components, such as paints. On the other hand, the Environmental Working Group
330 (EWG) affirm that sunscreens with inorganic UV-filters results a better choice for
331 marine environment than those with organic UV-filters (EWG, 2014), although they are
332 aware that effects of nanoparticles in the environment remains unknown. Because of the
333 effects of nanoparticles in the marine ecosystem are not fully understood, Jacobs et al.
334 (2010) considered that the use of these nanoparticles in sunscreens are morally
335 unacceptable. Consequently, investigations of sunscreens with “environmental-friendly”
336 formulations have increased in the last years (Danovaro et al., 2014). Since many
337 organisms in nature have developed its own photoprotective mechanisms the use of
338 natural components is being explored. Several types of secondary metabolites are

339 known to act as sunscreens in plants and animals, such as melanin (in humans),
340 scytonemin (in cyanobacteria), mycosporine and mycosporine-like amino acids
341 (MAA's) (with an wide phylogenetic distribution) and carotenoids which biosynthesis
342 can be UVB-inducible in cyanobacteria (Gao and Garcia-Pichel, 2011, and references
343 therein).

344 **4. Coastal Tourism trend and use of sunscreen: the Spain case**

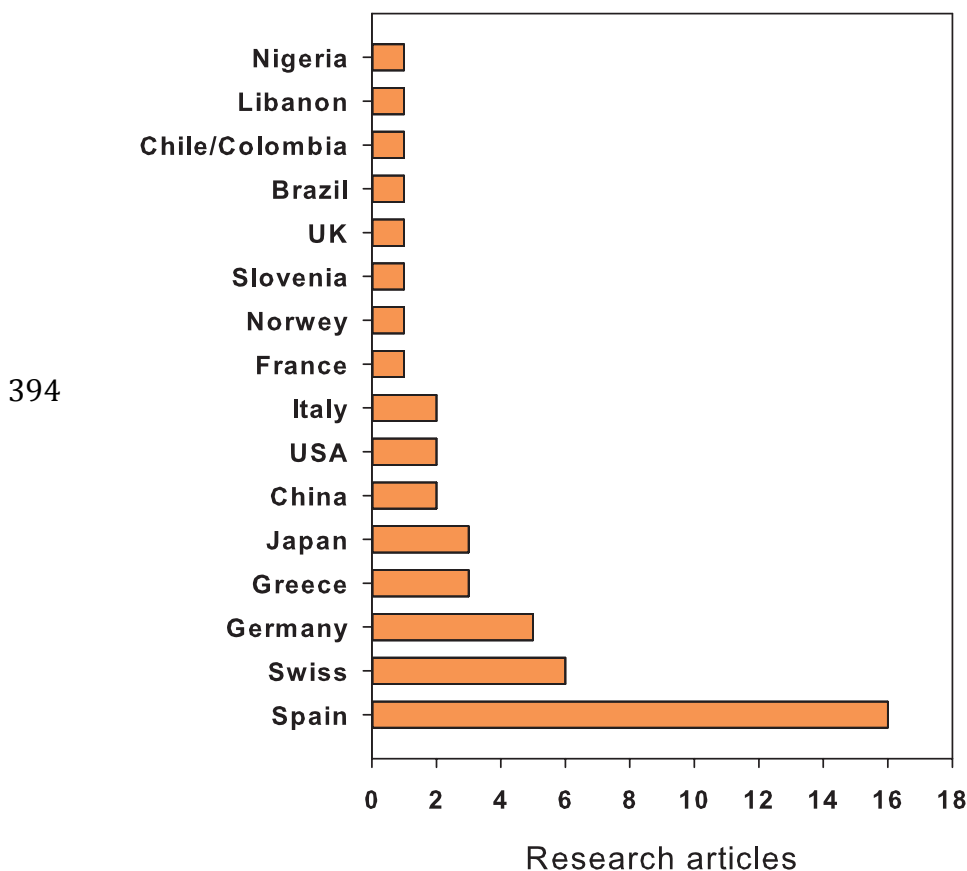
345 The world coastal-zone population is expected to grow from 1.2 billion people
346 (in 1990) up to 5.2 billion by the 2080 (Rabalais et al., 2009). According to the World
347 Tourism Organization (WTO), the Mediterranean coast received almost 30% of world
348 international tourist arrivals in 2013 (UNWTO World Tourism Barometer, 2014). With
349 220 million of tourists per year the Mediterranean region is one of the most visited
350 destinations in the world, and half of these visitors attend en masse to the Mediterranean
351 beaches (WWF Global). Moreover, it has been estimated that the Mediterranean region
352 could receive up to 264 million tourists in 2030 (World Tourism Organization
353 UNWTO, 2011).

354 In Spain, tourism is one of the mainstays of the country economy. It means
355 around 11 % of GDP and 13 % of employment, and contributes substantially to
356 offsetting the trade deficit. With a new record of foreign visitors (i.e. 64.9 million in
357 2014) (Turespaña, <http://www.iet.tourspain.es>), Spain has been consolidated as the
358 second-largest worldwide destination (in the OECD countries: organization for
359 Economic Co-operation and Development) in terms of tourist arrivals and receipts.
360 Tourist arrivals have increased by 93% in the period 2004 - 2008 (OECD Tourism
361 Trends and Policies, 2010), with more than 50 % of arrivals concentrated in the
362 Mediterranean coasts (Catalonia, Balearic Islands and Valencia) (Mantiñán and Solla,
363 2010). In fact, Balearic Islands is one of the most important tourist destinations in the
364 Mediterranean Sea (Cirer-Costa, 2012). The international tourist arrivals are increasing
365 every year, with more than 11 million of tourists arrivals in 2013, mostly concentrated
366 during summer season (Turespaña, <http://www.iet.tourspain.es>). In fact, it has been
367 considered like a second generation European mass tourist resort (Knowles and Curtis,
368 1999). With a 1.1 million of inhabitants, this income of visitors counts as more than 10
369 times the normal population of the islands

370 Associated with the growth of tourism activities, sun-care products present the

371 fastest growing sales rate globally, with the Western Europe as the largest market. Sun
372 protection is the most important segment of the sun care market with almost € 7.0
373 billion forecasted in 2014, a worldwide increase of 7 % per year over the last five years,
374 and with an average per capita consumption of 20 ml per year (Osterwalder et al.,
375 2014). Despite the high diversity of textures of sunscreens (e.g. lotions, spray, roll-on,
376 shake well types, etc.) lotions and creams represent approximately 60 % of the total
377 products introduced in the market. Spray format is also very popular in Europe with 20
378 % of presence in the market. Sunscreens with Solar Protection Factor (SPF) between 30
379 – 50 are produced in high quantities, and they represent the 50 - 60 % (Osterwalder et
380 al., 2014). Spain is the country with the highest consume of sunscreen per capita with
381 189 ml per year in 2012 (Osterwalder et al., 2014). Considering 47 million of
382 inhabitants it would represent a consumption of almost 9 million liters of sunscreen per
383 year. According to a survey carried out in Spain, almost 80 % of the population used
384 sunscreen to protect their skin against the UV radiation (Galán et al., 2011). This
385 percentage is significantly higher than in the United Kingdom (37 %) (Miles et al.,
386 2005) or Australia (27 %) (Dobbinson et al., 2008).

387 Despite this data, little is known about the effects of sun-care products on the
388 marine ecosystems. The use of these cosmetics has become popular since the second
389 half of 20th century; however, the first analyses of the UV-filters environmental
390 samples were made in 2002 (Lambropoulou et al., 2002). With less than 50 peer-review
391 scientific articles published to date (Figure 1), Spain is the country which has the
392 highest number of research investigations involving the analysis of environmental levels
393 of organic UV-filters (Figure 2).



395 Figure 2: Published research articles reporting environmental concentrations of organic
 396 UV-filters sorted by country.

397 **5. Conclusions and future perspectives**

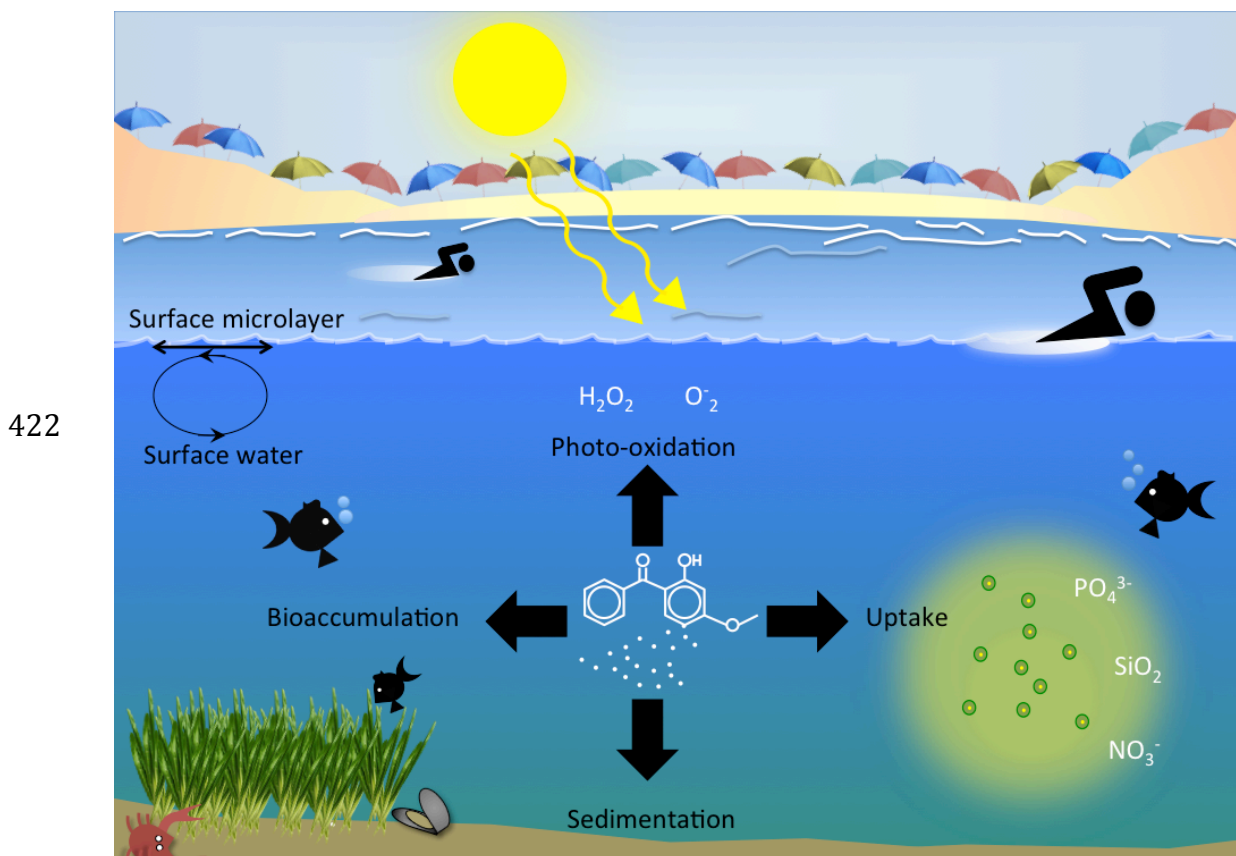
398 This review evaluates the environmental implications of commercial sunscreens
 399 and their main components as source of chemicals into the coastal ecosystem. Results
 400 presented here indicate that sunscreens are a significant source of chemicals that reach
 401 the sea and have potential ecological consequences on the coastal marine ecosystem.

402 Once in the water column, components released from sunscreens accumulate in
 403 the SML. Organic and inorganic UV-filters are photo-excited by sunlight generating
 404 elevated concentrations of reactive oxygen species with toxic effects on phytoplankton
 405 and being potentially bioaccumulative in the food web. Other components released from
 406 sunscreen (NO_3^- , NO_2^- , PO_4^{3-} , SiO_2 and NH_4^+) are easily dissolved in seawater and may
 407 stimulate algal growth (Figure 3).

408 Future investigations are needed to understand the real impact of this emerging

409 pollutant in the marine system, such as distribution and partitioning in the water
 410 column, dissolution and speciation of their main components, evaluation of the
 411 ecological significance of the input of nutrients, residence time and aging, persistence,
 412 accumulation and toxicity in the trophic chain. Additional ecotoxicological experiments
 413 are also needed to better understand the effects of these products in the marine
 414 environment. For example, new studies should evaluate the stress level and species
 415 succession in marine phytoplankton species and the effect on macroalgae and marine
 416 seagrasses. The marine macrophyte *Posidonia oceanica*, is an endemic seagrass from
 417 the Mediterranean Sea that is included in the Annex II of the Protocol of Barcelona
 418 Convention 1996 as an endangered marine species. The nearshore habitat of these
 419 marine plants, together with many other pelagic and benthic fauna, receives the
 420 influence of sunscreens and therefore its impact should be addressed.

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423 Figure 3: Conceptual diagram transfer of sunscreen derived-products.

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6. References

- Al-Bawab, A., Friberg, S.E., 2006. Some pertinent factors in skin care emulsion. *Adv. Colloid Interface Sci.*, Special Issue in Honor of Dr. K. L. Mittal 123–126, 313–322. doi:10.1016/j.cis.2006.06.004
- Allen, J.M., Gossett, C.J., Allen, S.K., 1996. Photochemical formation of singlet molecular oxygen in illuminated aqueous solutions of several commercially available sunscreen active ingredients. *Chem. Res. Toxicol.* 9, 605–609. doi:10.1021/tx950197m
- Amine, H., Gomez, E., Halwani, J., Casellas, C., Fenet, H., 2012. UV filters, ethylhexyl methoxycinnamate, octocrylene and ethylhexyl dimethyl PABA from untreated wastewater in sediment from eastern Mediterranean river transition and coastal zones. *Mar. Pollut. Bull.* 64, 2435–2442. doi:10.1016/j.marpolbul.2012.07.051
- Arukwe, A., Eggen, T., Möder, M., 2012. Solid waste deposits as a significant source of contaminants of emerging concern to the aquatic and terrestrial environments — A developing country case study from Owerri, Nigeria. *Sci. Total Environ.* 438, 94–102. doi:10.1016/j.scitotenv.2012.08.039
- Aschberger, K., Micheletti, C., Sokull-Klüttgen, B., Christensen, F.M., 2011. Analysis of currently available data for characterising the risk of engineered nanomaterials to the environment and human health — Lessons learned from four case studies. *Environ. Int.*, Special Issue: Environmental Fate and Effects of Nanoparticles 37, 1143–1156. doi:10.1016/j.envint.2011.02.005
- Bachelot, M., Li, Z., Munaron, D., Le Gall, P., Casellas, C., Fenet, H., Gomez, E., 2012. Organic UV filter concentrations in marine mussels from French coastal regions. *Sci. Total Environ.* 420, 273–279. doi:10.1016/j.scitotenv.2011.12.051
- Baker, T.J., Tyler, C.R., Galloway, T.S., 2014. Impacts of metal and metal oxide nanoparticles on marine organisms. *Environ. Pollut. Barking Essex 1987* 186C, 257–271. doi:10.1016/j.envpol.2013.11.014
- Balmer, M.E., Buser, H.-R., Müller, M.D., Poiger, T., 2005. Occurrence of Some Organic UV Filters in Wastewater, in Surface Waters, and in Fish from Swiss Lakes. *Env. Sci Technol* 39, 953–962. doi:10.1021/es040055r
- Barón, E., Gago-Ferrero, P., Gorga, M., Rudolph, I., Mendoza, G., Zapata, A.M., Díaz-Cruz, S., Barra, R., Ocampo-Duque, W., Páez, M., Darbra, R.M., Eljarrat, E., Barceló, D., 2013. Occurrence of hydrophobic organic pollutants (BFRs and UV-filters) in sediments from South America. *Chemosphere* 92, 309–316. doi:10.1016/j.chemosphere.2013.03.032
- Benedé, J.L., Chisvert, A., Giokas, D.L., Salvador, A., 2014a. Development of stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles and its analytical application to the determination of hydrophobic organic compounds in aqueous media. *J. Chromatogr. A* 1362, 25–33. doi:10.1016/j.chroma.2014.08.024
- Benedé, J.L., Chisvert, A., Salvador, A., Sánchez-Quiles, D., Tovar-Sánchez, A., 2014b. Determination of UV filters in both soluble and particulate fractions of seawaters by dispersive liquid–liquid microextraction followed by gas chromatography–mass

- spectrometry. *Anal. Chim. Acta* 812, 50–58. doi:10.1016/j.aca.2013.12.033
- Blüthgen, N., Zucchi, S., Fent, K., 2012. Effects of the UV filter benzophenone-3 (oxybenzone) at low concentrations in zebrafish (*Danio rerio*). *Toxicol. Appl. Pharmacol.* 263, 184–194. doi:10.1016/j.taap.2012.06.008
- Botta, C., Labille, J., Auffan, M., Borschneck, D., Miche, H., Cabié, M., Masion, A., Rose, J., Bottero, J.-Y., 2011. TiO₂-based nanoparticles released in water from commercialized sunscreens in a life-cycle perspective: Structures and quantities. *Environ. Pollut.* 159, 1543–1550. doi:10.1016/j.envpol.2011.03.003
- Bratkovics, S., Sapozhnikova, Y., 2011. Determination of seven commonly used organic UV filters in fresh and saline waters by liquid chromatography-tandem mass spectrometry. *Anal. Methods* 3, 2943–2950. doi:10.1039/c1ay05390f
- Buser, H.-R., Müller, M.D., Balmer, M.E., Poiger, T., Buerge, I.J., 2005. Stereoisomer Composition of the Chiral UV Filter 4-Methylbenzylidene Camphor in Environmental Samples. *Env. Sci Technol* 39, 3013–3019. doi:10.1021/es048265r
- Chen, J., Dong, X., Xin, Y., Zhao, M., 2011. Effects of titanium dioxide nano-particles on growth and some histological parameters of zebrafish (*Danio rerio*) after a long-term exposure. *Aquat. Toxicol.* 101, 493–499. doi:10.1016/j.aquatox.2010.12.004
- Chen, L., Hu, J.Y., Wang, S.Q., 2012. The role of antioxidants in photoprotection: a critical review. *J. Am. Acad. Dermatol.* 67, 1013–1024.
- Chen, L.L., Wang, S.Q., 2012. From the bottle to the skin: Challenges in evaluating antioxidants. *Photodermatol. Photoimmunol. Photomed.* 28, 228–234. doi:10.1111/j.1600-0781.2012.00674.x
- Chisvert, A., Salvador, A., 2007. UV Filters in Sunscreens and other Cosmetics. *Regulatory Aspects and Analytical Methods (3.1)*, in: *Analysis of Cosmetic Products*. Elsevier Science, Amsterdam, Holland, pp. 83–120.
- Cirer-Costa, J.C., 2012. The beginnings of tourism in Majorca. 1837-1914. *Ann. Tour. Res.* 39, 1779–1796. doi:10.1016/j.annals.2012.06.004
- Cuderman, P., Heath, E., 2007. Determination of UV filters and antimicrobial agents in environmental water samples. *Anal. Bioanal. Chem.* 387, 1343–1350. doi:10.1007/s00216-006-0927-y
- Danovaro, R., Bongiorno, L., Corinaldesi, C., Giovannelli, D., Damiani, E., Astolfi, P., Greci, L., Pusceddu, A., 2008. Sunscreens Cause Coral Bleaching by Promoting Viral Infections. *Environ. Health Perspect.* 116, 441–447. doi:10.1289/ehp.10966
- Danovaro, R., Corinaldesi, C., 2003. Sunscreen products increase virus production through prophage induction in marine bacterioplankton. *Microb. Ecol.* 45, 109–118. doi:10.1007/s00248-002-1033-0
- Danovaro, R., Damiani, E., Corinaldesi, C., 2014. Sunscreen Compositions. US2014170096 (A1).
- Davenport, J., Davenport, J.L., 2006. The impact of tourism and personal leisure transport on coastal environments: A review. *Estuar. Coast. Shelf Sci.* 67, 280–292.

doi:10.1016/j.ecss.2005.11.026

Díaz-Cruz, M.S., Barceló, D., 2009. Chemical analysis and ecotoxicological effects of organic UV-absorbing compounds in aquatic ecosystems. *TrAC Trends Anal. Chem.* 28, 708–717. doi:10.1016/j.trac.2009.03.010

Díaz-Cruz, S., Llorca, M., Barceló, D., 2008. Organic UV filters and their photodegradates, metabolites and disinfection by-products in the aquatic environment. *TrAC Trends Anal. Chem.* 27, 873–887. doi:10.1016/j.trac.2008.08.012

Diffey, B. I., 2005. Sunscreens and melanoma: the future looks bright. *Br. J. Dermatol.* 153, 378–381. doi:10.1111/j.1365-2133.2005.06729.x

Dobbinson, S.J., Wakefield, M.A., Jamsen, K.M., Herd, N.L., Spittal, M.J., Lipscomb, J.E., Hill, D.J., 2008. Weekend Sun Protection and Sunburn in Australia: Trends (1987–2002) and Association with SunSmart Television Advertising. *Am. J. Prev. Med.* 34, 94–101. doi:10.1016/j.amepre.2007.09.024

EWG 2014, n.d. Nanomaterials in Sunscreen EWG's 2014 Guide to Sunscreens [WWW Document]. URL <http://www.ewg.org/2014sunscreens/nanoparticles-in-sunscreens/> (accessed 9.23.14).

Farah K. Ahmed, 2008. Worldwide Regulation of UV Filters: Current Status and Future Trends, in: *Clinical Guide to Sunscreens and Photoprotection, Basic and Clinical Dermatology*. Informa Healthcare, pp. 65–82.

Farré, M., Barceló, D., 2012. Chapter 1 - Introduction to the Analysis and Risk of Nanomaterials in Environmental and Food Samples, in: Marinella Farré and Damià Barceló (Ed.), *Comprehensive Analytical Chemistry, Analysis and Risk of Nanomaterials in Environmental and Food Samples*. Elsevier, pp. 1–32.

Fent, K., Kunz, P.Y., Zenker, A., Rapp, M., 2010a. A tentative environmental risk assessment of the UV-filters 3-(4-methylbenzylidene-camphor), 2-ethyl-hexyl-4-trimethoxycinnamate, benzophenone-3, benzophenone-4 and 3-benzylidene camphor. *Mar. Environ. Res.* 69, S4–S6. doi:10.1016/j.marenvres.2009.10.010

Fent, K., Zenker, A., Rapp, M., 2010b. Widespread occurrence of estrogenic UV-filters in aquatic ecosystems in Switzerland. *Environ. Pollut.* 158, 1817–1824. doi:10.1016/j.envpol.2009.11.005

Forestier, S., Hansenne, I., Petitdemange, D., 1995. Cosmetic composition comprising the combination of a nanopigment of metal oxides and an antioxidant, and use thereof for protecting the skin and the hair. FR2708851 (A1).

Gago-Ferrero, P., Alonso, M.B., Bertozzi, C.P., Marigo, J., Barbosa, L., Cremer, M., Secchi, E.R., Azevedo, A., Lailson-Brito Jr., J., Torres, J.P.M., Malm, O., Eljarrat, E., Díaz-Cruz, M.S., Barceló, D., 2013a. First determination of UV filters in marine mammals. octocrylene levels in Franciscana dolphins. *Environ. Sci. Technol.* 47, 5619–5625. doi:10.1021/es400675y

Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2011a. Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV filters and their degradation products in sediments. *Anal. Bioanal. Chem.* 400, 2195–2204. doi:10.1007/s00216-011-4951-1

- Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2011b. Occurrence of multiclass UV filters in treated sewage sludge from wastewater treatment plants. *Chemosphere* 84, 1158–1165. doi:10.1016/j.chemosphere.2011.04.003
- Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2012. An overview of UV-absorbing compounds (organic UV filters) in aquatic biota. *Anal. Bioanal. Chem.* 404, 2597–2610. doi:10.1007/s00216-012-6067-7
- Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2013b. Multi-residue method for trace level determination of UV filters in fish based on pressurized liquid extraction and liquid chromatography–quadrupole-linear ion trap-mass spectrometry. *J. Chromatogr. A* 1286, 93–101. doi:10.1016/j.chroma.2013.02.056
- Gago-Ferrero, P., Mastroianni, N., Díaz-Cruz, M.S., Barceló, D., 2013c. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction–liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1294, 106–116. doi:10.1016/j.chroma.2013.04.037
- Galán, I., Rodríguez-Laso, Á., Díez-Gañán, L., Cámara, E., 2011. Prevalence and correlates of skin cancer risk behaviors in Madrid (Spain). *Gac. Sanit.* 25, 44–49. doi:10.1016/j.gaceta.2010.07.013
- Gao, L., Yuan, T., Zhou, C., Cheng, P., Bai, Q., Ao, J., Wang, W., Zhang, H., 2013. Effects of four commonly used UV filters on the growth, cell viability and oxidative stress responses of the *Tetrahymena thermophila*. *Chemosphere* 93, 2507–2513. doi:10.1016/j.chemosphere.2013.09.041
- Gao, Q., Garcia-Pichel, F., 2011. Microbial ultraviolet sunscreens. *Nat. Rev. Microbiol.* 9, 791–802. doi:10.1038/nrmicro2649
- Giokas, D.L., Sakkas, V.A., Albanis, T.A., 2004. Determination of residues of UV filters in natural waters by solid-phase extraction coupled to liquid chromatography–photodiode array detection and gas chromatography–mass spectrometry. *J. Chromatogr. A* 1026, 289–293. doi:10.1016/j.chroma.2003.10.114
- Giokas, D.L., Sakkas, V.A., Albanis, T.A., Lampropoulou, D.A., 2005. Determination of UV-filter residues in bathing waters by liquid chromatography UV-diode array and gas chromatography–mass spectrometry after micelle mediated extraction–solvent back extraction. *J. Chromatogr. A* 1077, 19–27. doi:10.1016/j.chroma.2005.04.074
- Giokas, D.L., Salvador, A., Chisvert, A., 2007. UV filters: From sunscreens to human body and the environment. *TrAC Trends Anal. Chem.* 26, 360–374. doi:10.1016/j.trac.2007.02.012
- Goksøyr, A., Tollefsen, K.E., Grung, M., Løken, K., Lie, E., Zenker, A., Fent, K., Schlabach, M., Huber, S., 2009. Balsa Raft Crossing the Pacific Finds Low Contaminant Levels. *Environ. Sci. Technol.* 43, 4783–4790. doi:10.1021/es900154h
- Gómez, M.J., Gómez-Ramos, M.M., Agüera, A., Mezcuca, M., Herrera, S., Fernández-Alba, A.R., 2009. A new gas chromatography/mass spectrometry method for the simultaneous analysis of target and non-target organic contaminants in waters. *J. Chromatogr. A* 1216, 4071–4082. doi:10.1016/j.chroma.2009.02.085

- Gondikas, A.P., Von Der Kammer, F., Reed, R.B., Wagner, S., Ranville, J.F., Hofmann, T., 2014. Release of TiO₂ nanoparticles from sunscreens into surface waters: A one-year survey at the old danube recreational lake. *Environ. Sci. Technol.* 48, 5415–5422. doi:10.1021/es405596y
- Gormsen, E., 1997. The impact of tourism on coastal areas. *GeoJournal* 42, 39–54. doi:10.1023/A:1006840622450
- Hall, C.M., 2001. Trends in ocean and coastal tourism: the end of the last frontier? *Ocean Coast. Manag., Trends in Ocean Industries* 44, 601–618. doi:10.1016/S0964-5691(01)00071-0
- Hanson, K.M., Gratton, E., Bardeen, C.J., 2006. Sunscreen enhancement of UV-induced reactive oxygen species in the skin. *Free Radic. Biol. Med.* 41, 1205–1212. doi:10.1016/j.freeradbiomed.2006.06.011
- Holick, M.F., 2004. Sunlight and vitamin D for bone health and prevention of autoimmune diseases, cancers, and cardiovascular disease. *Am. J. Clin. Nutr.* 80, 1678S–1688S.
- <http://www.iet.tourspain.es>, n.d. Tourspain website; <http://www.iet.tourspain.es> [WWW Document]. URL <http://www.iet.tourspain.es> (accessed 1.27.15).
- Hund-Rinke, K., Simon, M., 2006. Ecotoxic Effect of Photocatalytic Active Nanoparticles (TiO₂) on Algae and Daphnids (8 pp). *Environ. Sci. Pollut. Res.* 13, 225–232. doi:10.1065/espr2006.06.311
- Inbaraj, J.J., Bilski, P., Chignell, C.F., 2002. Photophysical and photochemical studies of 2-phenylbenzimidazole and UVB sunscreen 2-phenylbenzimidazole-5-sulfonic acid. *Photochem. Photobiol.* 75, 107–116.
- Jacobasch, C., Völker, C., Giebner, S., Völker, J., Alsenz, H., Potouridis, T., Heidenreich, H., Kayser, G., Oehlmann, J., Oetken, M., 2014. Long-term effects of nanoscaled titanium dioxide on the cladoceran *Daphnia magna* over six generations. *Environ. Pollut.* 186, 180–186. doi:10.1016/j.envpol.2013.12.008
- Jacobs, J.F., van de Poel, I., Osseweijer, P., 2010. Sunscreens with Titanium Dioxide (TiO₂) Nano-Particles: A Societal Experiment. *Nanoethics* 4, 103–113. doi:10.1007/s11569-010-0090-y
- Jansen, R., Osterwalder, U., Wang, S.Q., Burnett, M., Lim, H.W., 2013a. Photoprotection: Part II. Sunscreen: Development, efficacy, and controversies. *J. Am. Acad. Dermatol.* 69, 867.e1–867.e14. doi:10.1016/j.jaad.2013.08.022
- Jansen, R., Wang, S.Q., Burnett, M., Osterwalder, U., Lim, H.W., 2013b. Photoprotection: Part I. Photoprotection by naturally occurring, physical, and systemic agents. *J. Am. Acad. Dermatol.* 69, 853.e1–853.e12. doi:10.1016/j.jaad.2013.08.021
- Jovanović, B., 2015. Review of titanium dioxide nanoparticle phototoxicity: Developing a phototoxicity ratio to correct the endpoint values of toxicity tests. *Environ. Toxicol. Chem.* n/a–n/a. doi:10.1002/etc.2891
- Jurado, A., Gago-Ferrero, P., Vázquez-Suñé, E., Carrera, J., Pujades, E., Díaz-Cruz, M.S., Barceló, D., 2014. Urban groundwater contamination by residues of UV filters. *J.*

- Hazard. Mater. 271, 141–149. doi:10.1016/j.jhazmat.2014.01.036
- Kaiser, D., Sieratowicz, A., Zielke, H., Oetken, M., Hollert, H., Oehlmann, J., 2012. Ecotoxicological effect characterisation of widely used organic UV filters. *Environ. Pollut.* 163, 84–90. doi:10.1016/j.envpol.2011.12.014
- Kameda, Y., Kimura, K., Miyazaki, M., 2011. Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes. *Environ. Pollut.* 159, 1570–1576. doi:10.1016/j.envpol.2011.02.055
- Kamerow, D., 2014. My new year's wish is for an effective sunscreen. *BMJ Online* 349. doi:10.1136/bmj.g7729
- Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J., 2008. The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Water Res.* 42, 3498–3518. doi:10.1016/j.watres.2008.04.026
- Kawaguchi, M., Ito, R., Honda, H., Endo, N., Okanouchi, N., Saito, K., Seto, Y., Nakazawa, H., 2008. Simultaneous analysis of benzophenone sunscreen compounds in water sample by stir bar sorptive extraction with in situ derivatization and thermal desorption–gas chromatography–mass spectrometry. *J. Chromatogr. A* 1200, 260–263. doi:10.1016/j.chroma.2008.05.084
- Kim, S., Choi, K., 2014. Occurrences, toxicities, and ecological risks of benzophenone-3, a common component of organic sunscreen products: A mini-review. *Environ. Int.* 70, 143–157. doi:10.1016/j.envint.2014.05.015
- Knowles, T., Curtis, S., 1999. The market viability of European mass tourist destinations. A post-stagnation life-cycle analysis. *Int. J. Tour. Res.* 1, 87–96. doi:10.1002/(SICI)1522-1970(199903/04)1:2<87::AID-JTR135>3.0.CO;2-6
- Labille, J., Feng, J., Botta, C., Borschneck, D., Sammut, M., Cabie, M., Auffan, M., Rose, J., Bottero, J.-Y., 2010. Aging of TiO₂ nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment. *Environ. Pollut.* 158, 3482–3489. doi:10.1016/j.envpol.2010.02.012
- Laborda, F., Bolea, E., Jiménez-Lamana, J., 2014. Single Particle Inductively Coupled Plasma Mass Spectrometry: A Powerful Tool for Nanoanalysis. *Anal. Chem.* 86, 2270–2278. doi:10.1021/ac402980q
- Lambropoulou, D., Giokas, D., Sakkas, V., Albanis, T., Karayannis, M., 2002. Gas chromatographic determination of 2-hydroxy-4-methoxybenzophenone and octyldimethyl-p-aminobenzoic acid sunscreen agents in swimming pool and bathing waters by solid-phase microextraction. *J. Chromatogr. A* 967, 243–253. doi:10.1016/S0021-9673(02)00781-1
- Langford, K.H., Thomas, K.V., 2008. Inputs of chemicals from recreational activities into the Norwegian coastal zone. *J. Environ. Monit.* 10, 894–898. doi:10.1039/B806198J
- Lee, S., Bi, X., Reed, R.B., Ranville, J.F., Herckes, P., Westerhoff, P., 2014. Nanoparticle Size Detection Limits by Single Particle ICP-MS for 40 Elements. *Environ. Sci. Technol.* 48, 10291–10300. doi:10.1021/es502422v

- Lesser, M.P., 2006. Oxidative stress in marine environments: biochemistry and physiological ecology. *Annu. Rev. Physiol.* 68, 253–278. doi:10.1146/annurev.physiol.68.040104.110001
- Lewicka, Z.A., Benedetto, A.F., Benoit, D.N., Yu, W.W., Fortner, J.D., Colvin, V.L., 2011. The structure, composition, and dimensions of TiO₂ and ZnO nanomaterials in commercial sunscreens. *J. Nanoparticle Res.* 13, 3607–3617. doi:10.1007/s11051-011-0438-4
- Li, S., Wallis, L.K., Ma, H., Diamond, S.A., 2014. Phototoxicity of TiO₂ nanoparticles to a freshwater benthic amphipod: Are benthic systems at risk? *Sci. Total Environ.* 466–467, 800–808. doi:10.1016/j.scitotenv.2013.07.059
- Li, W., Ma, Y., Guo, C., Hu, W., Liu, K., Wang, Y., Zhu, T., 2007. Occurrence and behavior of four of the most used sunscreen UV filters in a wastewater reclamation plant. *Water Res.* 41, 3506–3512. doi:10.1016/j.watres.2007.05.039
- López-Heras, I., Madrid, Y., Cámara, C., 2014. Prospects and difficulties in TiO₂ nanoparticles analysis in cosmetic and food products using asymmetrical flow field-flow fractionation hyphenated to inductively coupled plasma mass spectrometry. *Talanta* 124, 71–78. doi:10.1016/j.talanta.2014.02.029
- Luo, Z., Wang, Z., Xu, B., Sarakiotis, I.L., Laing, G.D., Yan, C., 2014. Measurement and characterization of engineered titanium dioxide nanoparticles in the environment. *J. Zhejiang Univ. Sci. A* 15, 593–605. doi:10.1631/jzus.A1400111
- Magi, E., Di Carro, M., Scapolla, C., Nguyen, K.T.N., 2012. Stir bar sorptive extraction and LC-MS/MS for trace analysis of UV filters in different water matrices. *Chromatographia* 75, 973–982. doi:10.1007/s10337-012-2202-z
- Ma, H., Brennan, A., Diamond, S.A., 2012. Phototoxicity of TiO₂ nanoparticles under solar radiation to two aquatic species: *Daphnia magna* and Japanese medaka. *Environ. Toxicol. Chem.* 31, 1621–1629. doi:10.1002/etc.1858
- Manaia, E.B., Kaminski, R.C.K., Corrêa, M.A., Chiavacci, L.A., 2013. Inorganic UV filters. *Braz. J. Pharm. Sci.* 49, 201–209. doi:10.1590/S1984-82502013000200002
- Mansfield, C.M., Alloy, M.M., Hamilton, J., Verbeck, G.F., Newton, K., Klaine, S.J., Roberts, A.P., 2015. Photo-induced toxicity of titanium dioxide nanoparticles to *Daphnia magna* under natural sunlight. *Chemosphere* 120, 206–210. doi:10.1016/j.chemosphere.2014.06.075
- Mantiñán, M.J.P., Solla, X.M.S., 2010. Impact of Tourism on Coastal Towns: From Improvisation to Planification. *Open Urban Stud. J.* 3, 21–27.
- Miles, A., Waller, J., Hiom, S., Swanston, D., 2005. SunSmart? Skin cancer knowledge and preventive behaviour in a British population representative sample. *Health Educ. Res.* 20, 579–585. doi:10.1093/her/cyh010
- Miller, D., Wiener, E.-M., Turowski, A., Thunig, C., Hoffmann, H., 1999. O/W emulsions for cosmetics products stabilized by alkyl phosphates — rheology and storage tests. *Colloids Surf. Physicochem. Eng. Asp.* 152, 155–160. doi:10.1016/S0927-7757(98)00630-X

- Miller, R.J., Lenihan, H.S., Muller, E.B., Tseng, N., Hanna, S.K., Keller, A.A., 2010. Impacts of Metal Oxide Nanoparticles on Marine Phytoplankton. *Env. Sci Technol* 44, 7329–7334. doi:10.1021/es100247x
- Minetto, D., Libralato, G., Volpi Ghirardini, A., 2014. Ecotoxicity of engineered TiO₂ nanoparticles to saltwater organisms: An overview. *Environ. Int.* 66, 18–27. doi:10.1016/j.envint.2014.01.012
- Nguyen, K.T.N., Scapolla, C., Di Carro, M., Magi, E., 2011. Rapid and selective determination of UV filters in seawater by liquid chromatography-tandem mass spectrometry combined with stir bar sorptive extraction. *Talanta* 85, 2375–2384. doi:10.1016/j.talanta.2011.07.085
- OECD Tourism Trends and Policies 2010, n.d. Tourism - OECD; <http://www.oecd.org/cfe/tourism/oecd tourism trends policies 2010.htm> [WWW Document]. URL <http://www.oecd.org/cfe/tourism/oecd tourism trends policies 2010.htm> (accessed 8.25.14).
- Oliveira, H.M., Segundo, M.A., Lima, J.L.F.C., Miró, M., Cerdà, V., 2010. On-line renewable solid-phase extraction hyphenated to liquid chromatography for the determination of UV filters using bead injection and multisyringe-lab-on-valve approach. *J. Chromatogr. A* 1217, 3575–3582. doi:10.1016/j.chroma.2010.03.035
- Osterwalder, U., Sohn, M., Herzog, B., 2014. Global state of sunscreens. *Photodermatol. Photoimmunol. Photomed.* 30, 62–80. doi:10.1111/phpp.12112
- Paredes, E., Perez, S., Rodil, R., Quintana, J.B., Beiras, R., 2014. Ecotoxicological evaluation of four UV filters using marine organisms from different trophic levels *Isochrysis galbana*, *Mytilus galloprovincialis*, *Paracentrotus lividus*, and *Siriella armata*. *Chemosphere* 104, 44–50. doi:10.1016/j.chemosphere.2013.10.053
- Pedrouzo, M., Borrull, F., Marcé, R.M., Pocurull, E., 2009. Ultra-high-performance liquid chromatography-tandem mass spectrometry for determining the presence of eleven personal care products in surface and wastewaters. *J. Chromatogr. A* 1216, 6994–7000. doi:10.1016/j.chroma.2009.08.039
- Pedrouzo, M., Borrull, F., Marcé, R.M., Pocurull, E., 2010. Stir-bar-sorptive extraction and ultra-high-performance liquid chromatography-tandem mass spectrometry for simultaneous analysis of UV filters and antimicrobial agents in water samples. *Anal. Bioanal. Chem.* 397, 2833–2839.
- Piccinno, F., Gottschalk, F., Seeger, S., Nowack, B., 2012. Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *J. Nanoparticle Res.* 14, 1–11. doi:10.1007/s11051-012-1109-9
- Pintado-Herrera, M.G., González-Mazo, E., Lara-Martín, P.A., 2013. Environmentally friendly analysis of emerging contaminants by pressurized hot water extraction-stir bar sorptive extraction-derivatization and gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* 405, 401–411. doi:10.1007/s00216-012-6453-1
- Plagellat, C., Kupper, T., Furrer, R., de Alencastro, L.F., Grandjean, D., Tarradellas, J., 2006. Concentrations and specific loads of UV filters in sewage sludge originating from a monitoring network in Switzerland. *Chemosphere* 62, 915–925.

doi:10.1016/j.chemosphere.2005.05.024

Plass, J., Emeis, D., Blümich, B., 2001. ³¹P nuclear magnetic resonance studies on alkyl phosphate emulsifiers in cosmetic oil-in-water emulsions. *J. Surfactants Deterg.* 4, 379–384. doi:10.1007/s11743-001-0191-3

Poiger, T., Buser, H.-R., Balmer, M.E., Bergqvist, P.-A., Müller, M.D., 2004. Occurrence of UV filter compounds from sunscreens in surface waters: regional mass balance in two Swiss lakes. *Chemosphere* 55, 951–963. doi:10.1016/j.chemosphere.2004.01.012

Rabalais, N.N., Turner, R.E., Díaz, R.J., Justić, D., 2009. Global change and eutrophication of coastal waters. *ICES J. Mar. Sci. J. Cons.* 66, 1528–1537. doi:10.1093/icesjms/fsp047

Ricking, M., Schwarzbauer, J., Franke, S., 2003. Molecular markers of anthropogenic activity in sediments of the Havel and Spree Rivers (Germany). *Water Res.* 37, 2607–2617. doi:10.1016/S0043-1354(03)00078-2

Rik Roelandts, 2008. History of Photoprotection, in: *Clinical Guide to Sunscreens and Photoprotection, Basic and Clinical Dermatology*. Informa Healthcare, pp. 1–10.

Rodil, R., Moeder, M., 2008. Development of a simultaneous pressurised-liquid extraction and clean-up procedure for the determination of UV filters in sediments. *Anal. Chim. Acta* 612, 152–159. doi:10.1016/j.aca.2008.02.030

Rodil, R., Quintana, J.B., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2009a. Multi-residue analytical method for the determination of emerging pollutants in water by solid-phase extraction and liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1216, 2958–2969. doi:10.1016/j.chroma.2008.09.041

Rodil, R., Schrader, S., Moeder, M., 2009b. Pressurised membrane-assisted liquid extraction of UV filters from sludge. *J. Chromatogr. A* 1216, 8851–8858. doi:10.1016/j.chroma.2009.10.058

Rodil, R., Schrader, S., Moeder, M., 2009c. Non-porous membrane-assisted liquid–liquid extraction of UV filter compounds from water samples. *J. Chromatogr. A* 1216, 4887–4894. doi:10.1016/j.chroma.2009.04.042

Salvador, A., Chisvert, A., 2005. Sunscreen analysis: A critical survey on UV filters determination. *Anal. Chim. Acta* 537, 1–14. doi:10.1016/j.aca.2005.01.055

Sánchez-Brunete, C., Miguel, E., Albero, B., Tadeo, J.L., 2011. Analysis of salicylate and benzophenone-type UV filters in soils and sediments by simultaneous extraction cleanup and gas chromatography–mass spectrometry. *J. Chromatogr. A* 1218, 4291–4298. doi:10.1016/j.chroma.2011.05.030

Sánchez-Quiles, D., Tovar-Sánchez, A., 2014. Sunscreens as a Source of Hydrogen Peroxide Production in Coastal Waters. *Environ. Sci. Technol.* 48, 9037–9042. doi:10.1021/es5020696

Sánchez-Quiles, D., Tovar-Sánchez, A., Horstkotte, B., 2013. Titanium determination by multisyringe flow injection analysis system and a liquid waveguide capillary cell in solid and liquid environmental samples. *Mar. Pollut. Bull.* 76, 89–94.

doi:10.1016/j.marpolbul.2013.09.024

Santos, A.J.M., Miranda, M.S., Esteves da Silva, J.C.G., 2012. The degradation products of UV filters in aqueous and chlorinated aqueous solutions. *Water Res.* 46, 3167–3176. doi:10.1016/j.watres.2012.03.057

Sieratowicz, A., Kaiser, D., Behr, M., Oetken, M., Oehlmann, J., 2011. Acute and chronic toxicity of four frequently used UV filter substances for *Desmodesmus subspicatus* and *Daphnia magna*. *J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng.* 46, 1311–1319. doi:10.1080/10934529.2011.602936

Sobek, A., Bejgarn, S., Rudén, C., Molander, L., Breitholtz, M., 2013. In the shadow of the Cosmetic Directive — Inconsistencies in EU environmental hazard classification requirements for UV-filters. *Sci. Total Environ.* 461–462, 706–711. doi:10.1016/j.scitotenv.2013.05.074

Sun, T.Y., Gottschalk, F., Hungerbühler, K., Nowack, B., 2014. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. *Environ. Pollut.* 185, 69–76. doi:10.1016/j.envpol.2013.10.004

Tarazona, I., Chisvert, A., León, Z., Salvador, A., 2010. Determination of hydroxylated benzophenone UV filters in sea water samples by dispersive liquid-liquid microextraction followed by gas chromatography-mass spectrometry. *J. Chromatogr. A* 1217, 4771–4778. doi:10.1016/j.chroma.2010.05.047

Tarazona, I., Chisvert, A., Salvador, A., 2014. Development of a gas chromatography-mass spectrometry method for the determination of ultraviolet filters in beach sand samples. *Anal. Methods* 6, 7772–7780. doi:10.1039/C4AY01403K

Tashiro, Y., Kameda, Y., 2013. Concentration of organic sun-blocking agents in seawater of beaches and coral reefs of Okinawa Island, Japan. *Mar. Pollut. Bull.* 77, 333–340. doi:10.1016/j.marpolbul.2013.09.013

Tovar-Sánchez, A., Sánchez-Quiles, D., Basterretxea, G., Benedé, J.L., Chisvert, A., Salvador, A., Moreno-Garrido, I., Blasco, J., 2013. Sunscreen Products as Emerging Pollutants to Coastal Waters. *PLoS ONE* 8, e65451. doi:10.1371/journal.pone.0065451

Trenholm, R.A., Vanderford, B.J., Drewes, J.E., Snyder, S.A., 2008. Determination of household chemicals using gas chromatography and liquid chromatography with tandem mass spectrometry. *J. Chromatogr. A* 1190, 253–262. doi:10.1016/j.chroma.2008.02.032

Tsui, M.M.P., Leung, H.W., Lam, P.K.S., Murphy, M.B., 2014. Seasonal occurrence, removal efficiencies and preliminary risk assessment of multiple classes of organic UV filters in wastewater treatment plants. *Water Res.* 53, 58–67. doi:10.1016/j.watres.2014.01.014

UNWTO World Tourism Barometer; 2014. UNWTO World Tourism Barometer; <http://mkt.unwto.org/en/barometer> [WWW Document]. URL <http://mkt.unwto.org/en/barometer>

Urbach, F., 2001. The historical aspects of sunscreens. *J. Photochem. Photobiol. B, ESP Conference on Photoprotection* 64, 99–104. doi:10.1016/S1011-1344(01)00202-0

US EPA National Center for Environmental Assessment, R.T.P.N., Powers, C., n.d. Nanomaterial Case Studies: Nanoscale Titanium Dioxide in Water Treatment and in Topical Sunscreen (Final) [WWW Document]. URL <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=230972> (accessed 9.1.14).

Vidal, L., Chisvert, A., Canals, A., Salvador, A., 2010. Ionic liquid-based single-drop microextraction followed by liquid chromatography-ultraviolet spectrophotometry detection to determine typical UV filters in surface water samples. *Talanta* 81, 549–555. doi:10.1016/j.talanta.2009.12.042

What's Hot around the Globe: Insights on Personal Care Products. Global Service Studies Website; [WWW Document], 2007. URL <http://kr.en.nielsen.com/reports/GlobalServiceStudies.shtml>

Wick, A., Fink, G., Ternes, T.A., 2010. Comparison of electrospray ionization and atmospheric pressure chemical ionization for multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1217, 2088–2103. doi:10.1016/j.chroma.2010.01.079

World Tourism Organization UNWTO;, 2011. Tourism Towards 2030 / Global Overview; <http://www.e-unwto.org/content/w45127/?p=189899a5998f428f99f66ca0e17d2218> [WWW Document]. URL <http://www.e-unwto.org/content/w45127/?p=189899a5998f428f99f66ca0e17d2218>

WWF Global, n.d. Key threats in the Mediterranean region (<http://www.mediterranean.panda.org/threats/>) [WWW Document]. URL <http://www.mediterranean.panda.org/threats/> (accessed 11.2.14).

Zenker, A., Schmutz, H., Fent, K., 2008. Simultaneous trace determination of nine organic UV-absorbing compounds (UV filters) in environmental samples. *J. Chromatogr. A* 1202, 64–74. doi:10.1016/j.chroma.2008.06.041

Zucchi, S., Blüthgen, N., Ieronimo, A., Fent, K., 2011a. The UV-absorber benzophenone-4 alters transcripts of genes involved in hormonal pathways in zebrafish (*Danio rerio*) eleuthero-embryos and adult males. *Toxicol. Appl. Pharmacol.* 250, 137–146. doi:10.1016/j.taap.2010.10.001

Zucchi, S., Oggier, D.M., Fent, K., 2011b. Global gene expression profile induced by the UV-filter 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC) in zebrafish (*Danio rerio*). *Environ. Pollut., Nitrogen Deposition, Critical Loads and Biodiversity* 159, 3086–3096. doi:10.1016/j.envpol.2011.04.013

