UV-Filters Risk for Coastal Environments

Subjects: Marine & Freshwater Biology Contributor: Letizia Marsili

Considering the rapid growth of tourism in recent years and the acknowledgement that exposure to solar UV radiation may cause skin cancer, sunscreens have been widely used by beachgoers in recent decades. UV filters contained in sunscreens were recently identified as emerging pollutants in coastal waters since they accumulate in the marine environment with different adverse effects. In fact, direct and/or indirect exposure to these components was proven to be harmful and eventually toxic to many invertebrate and vertebrate marine species.

Keywords: sunscreens ; UV filters ; nanoparticles ; coastal areas ; coral reef ; ecotoxicology

1. Introduction

During the last decade, tourism has seen massive growth and is among the economic sectors expected to experience constant development in the future. It was estimated that by 2035, the rate of global tourism will increase by 179%, and is set to generate substantial anthropic stress on natural environments^[1]. Water environments are at high risk, and plenty of research has been devoted to studying them: fragile balances regulate these environments, particularly in the coastal areas, for they are very rich in biodiversity and the ecosystem services provided by these areas sustain half of the planet population^[2]. Coastal tourism, and the related recreational activities, have led to a massive use of photoprotective personal care products (PCPs), which are highly and widely recommended to prevent skin damage from sun exposure^{[2][A]} [5], resulting in a direct input from swimming and bathing (non-point sources). These inputs, together with industrial wastewater discharges (point sources)[G|[Z][8], are capable of starting decay processes, irreversible at times[5]. In fact, coastal tourism is acknowledged as a source of impact on shallow-water marine habitats^[1], as well as lakes and rivers^[9] ^[10]. This means that nowadays there is a gap in judging the threat currently posed to the environment. Nonetheless, it was evaluated that, during in-water activities, at least 25% of sunscreens and PCPs applied to the skin get washed off^[11]. A study carried out in France estimated that a sample of 3000 beachgoers applied, on average, 52.5 kg of sunscreen per day, releasing 15.7 kg of it into the water^[12]. Since the widespread use of photoprotective PCPs, UV filters contained in sunscreens have become emerging contaminants in various environments. Only in recent years, the scientific community has started studying and investigating the causes and the effects of their accumulation in different ecosystems^{[3][13][14][15]}.

Sunscreen lotions are defined as PCPs containing UV filters, substances whose main function is to reflect, to refract, and to dissipate the wavelengths of sunlight considered harmful to human skin (UVA 320–400 nm and UV-B 280–320 nm). These lotions are designed for external application and the UV filters contained in the general PCP formula can be distinguished into organic and inorganic^[16].

Inorganic (also referred to as physical or mineral) filters provide filtering action against sunlight via two mechanisms: (1) the crystals refract and scatter a significant amount of the incoming radiation, and (2) the molecules themselves get to an excited state and then de-excite the same way as organic filters. These cycles of excitement and de-excitement entail a collateral photocatalytic activity, which is capable of producing reactive oxygen species (ROS), such as $O_2^{-\bullet}$, HO•, and $H_2O_2^{[17]}$. There are only two mineral filters widely approved and used around the world: titanium dioxide (TiO₂) and zinc oxide (ZnO), which can be used in both micrometric (TiO₂ and ZnO) and nanometric form (n-TiO₂ and n-ZnO). In the latter, the particles can be referred to as engineered nanoparticles (NPs or ENPs) and, if they are made of TiO₂, they are often coated with inert compounds to avoid undesired chemical reactions capable of skin damage^[18]. The coating often has one or two layers: the innermost, which is made of an inert material, e.g., alumina (Al₂O₃), aluminum hydroxide (Al(OH)₃) or silica (SiO₂)^[19], and the outer, e.g., silicone, which is optional and used to give hydrophobic properties to improve the blending capacities of TiO₂^[20].

Apart from UV filters, sunscreen lotions contain other ingredients such as preservatives, emulsifiers, colorants, foams, and perfumes^[4].

2. Abiotic Compartment

The most analyzed matrices to evaluate the behavior of UV filters are waters, sediments, and SML (surface microlayer). Water samples are used to evaluate the water solubility of the substances examined and the relative concentrations^{[21][22]} [^{23][24][25]}, while sediments and SML are used because they are more suitable for the identification of lipophilic compounds released into the environment^{[4][3][26]}.

Once leached into the water, they undergo further modifications since the external silicone layer can be easily degraded in slightly acidic (pH = 5) or slightly alkaline (pH = 9) waters^[20]. As time passes and the surface becomes more and more degraded, NPs can enter into suspension from 5% to over 30% of the total amount of sunscreen dispersed in water^{[19][27]}. The presence of organic matter in water represents an important contribution for the stabilization of the particles of n-TiO₂, which, once dispersed in water, may remain isolated or form aggregates together with macromolecules capable of forming complexes (e.g., humic acids)^{[28][29]} that endure in the environment. Moreover, there is evidence that salinity and pH play a role in leading NPs to aggregate and to descend the water column until they reach the bottom, where they may lay and eventually sediment^[19].

The main negative side of inorganic UV filters is their ability to transfer the absorbed energy to other surrounding molecules, causing ROS formation. These oxygen compounds, characterized by a high reactivity, cause oxidative stress in organisms exposed to higher concentrations. In particular, the photocatalytic activity of TiO_2 is also linked to the size of the particles used in the formulation: the microparticles have a moderate reactivity, which does not require countermeasures beyond the respect of a maximum percentage in the formulation; nanoparticles, on the other hand, are much more reactive and therefore require a coating^{[19][30][31]}.

Organic UV filters tend to be more concentrated on the SML and could, therefore, influence the availability of sunlight for photosynthetic organisms, a phenomenon which would be especially harmful in areas where barrier reefs are present^[11] ^[32]. This happens because some organic UV filters have photocatalytic activity, a feature that makes them co-responsible for the overproduction of ROS in aquatic environments^{[33][34]}. The main responsible organic UV filters for ROS production in aquatic environment are octinoxate (EHMC), octocrylene (OCR), 4-aminobenzoic acid (PABA), and 2-ethylhexyl 4-(dimethylamino)benzoate (OD-PABA). In this context, benzophenones (particularly BP-3 and BP-8) and ethylhexyl salicylate (OCS) are more suitable because they seem to be incapable of forming singlet oxygen or other ROS when exposed to light^[33]. In a well-lit environment, sunscreens can also undergo photodegradation, often generating less toxic compounds than the original UV filter: benzophenone derivatives showed, in laboratory studies, a modest genotoxic potential if present in concentrations of >250 ng/L, comparable to those that they are found in crowded parts of the coast or areas with low water exchange^{[35][36][37]}. Other UV filters, such as OD-PABA, EHMC and iso-amylmethoxy-cinnamate (IAMC), are overall less toxic, especially if exposed to intense illumination due to their higher photolability, when compared to the previous case^{[37][38]}.

3. Biotic Compartment

Table 1 summarizes recent studies carried out on the exposure of various organisms to UV filters and the effects of these exposures.

UV filter(s)	Organism(s)	Exposure Conditions	Effects	Refe
4-MBC BP-3 BP-4 EHMC	Mediterranean mussel (Mytilus galloprovincialis), sea urchin (Paracentrotus lividus)	EC ₅₀	EHMC and 4-MBC toxicity assessed from 4–5 mg/L, followed by BP-3 and finally BP-4	[
n-TiO2	Mediterranean mussel (Mytilus galloprovincialis)	From 0.05 to 5 mg/L for 24 h	Cellular damage NRR in hemocytes and digestive glands; stimulated glutathione-S-transferase (GST)	[
n-TiO2	Mediterranean mussel (Mytillus galloprovincialis)	From 2.8 to 280 µg/L for 24 h	Adaptive response in gills at 28 µg/L; oxidative stress and neurotoxicity over 280 µg/L	[
n-TiO2	Marine abalone (Haliotis diversicolor supertexta)	Acute toxicity stress: from 0.1 to 10 mg/L for 96 h	Oxidative stress: SOD increased (1mg/L), GSH decreased (1mg/L), LPO dose-dependent increase	[
n-TiO2	Lungworm (Arenicola marina)	Sub-lethal OECD/ASTM 1990 acute toxicity test	Decrease in casting rate; increase in cellular damage (NRR); DNA damage in coelomocytes	[

Table 1. Effects of various UV filters from different studies.

n-ZnO	Sea urchin (Paracentrotus lividus)	21-day exposure via food to reach 10 mg Zn/kg food	Damages to immune cells (33% of damaged nucleus); transmissible effects to offspring (75.5% of malformed larvae)	Į
4-MBC	Senegalese sole (Solea senegalensis)	Mortality and growth assessment 96 h egg exposure from 0.235 to 0.935 mg/L; biochemical markers from 0.068 to 0.360 mg/L	Induced mortality and malformations in a dose-response manner; reduced growth with increasing concentrations; increased activity of AChE on larvae exposed to 0.085mg/L; significantly lower LDH activity (p b 0.05); swimming behavior was affected by 4-MBC at low concentrations.	[
BP-1 BP-2 BP-3 BP-4 BP-7 BP-8	Marine bacterium (Photobacterium phosphoreum) and planktonic crustacean (Daphnia magna)	EC ₅₀ protocol and QSAR modelling	Toxicity evaluated for both species	[
PBSA	Rainbow trout (Oncorhynchus mykiss)	21 and 42 days; from 1 to 1000 μg/L	Increased activity of P450 cytochromes	ſ
4-MBC BP-3 BMDBM EHMC OCR HMS	Ciliate (Tetrahymena thermophila)	IC ₅₀	4-MBC, BP-3 and BMDBM could significantly inhibit the activity of the MXR system, IC ₅₀ values of 4-MBC, BP-3, and BMDBM were 23.54, 40.59, and 26.37 IM	[
BP 2-HBP BP-3 BP-4	Bioluminescent bacterium (<i>Vibrio fischeri</i>) in vitro and zebrafish (<i>Danio rerio</i>) larvae in vitro	EC ₅₀ , SOS/umu assay and yeast estrogen screen assay (YES assay)	Luminescent bacteria toxicity, expressed as $logEC_{50}$, increased with the lipophilicity ($logK_{ow}$) of BP-derived UV filters; estrogenic activity in dose- effect relationship. <i>V. fischeri</i> toxicity order is BP-3 > 2-HBP > BP > BP-4	[
BP-1 BP-3	Green alga (Chlamydomonas reinhardtii)	Response surface methodologies (RSM)	Exposure to the combined BP-1 and BP-3 negatively affected cell growth and pigments production, with dose- dependent inhibition, affecting the photosynthesis process	[
BP-1 BP-2 3-BC Et-PABA	Fathead minnow (Pimephales promelas)	14-day BP-1 from 8.9 to 4919.4 μg/L; BP-2 from 10.3 to 8782.9 μg/L; 3BC from 8.7 to 952.5 μg/L e Et-PABA from 6.9 to 4394 μg/L	Induction of vitellogenin: 3-BC from 3 μ g/L and BP-2 from 1.2 mg/L caused feminization in male fish, alteration of gonads in male and female fish, and decrease in fertility and reproduction	[

BP-3	Zebrafish (<i>Danio rerio</i>)	Fish and embryos were exposed for 14 days and 120 h post-fertilization, respectively, to 2.4–312 µg/L and 8.2–438 µg/L BP-3.	BP-3 was partly transformed to BP-1 and both compounds were accumulated in adult fish; BP-3 exposure led to similar alterations of gene expression in both adult fish and eleuthero embryos with antiandrogenic activity	Į
BP-3	Japanese medaka (Oryzias latipes)	14 days from 0 to 90 μg/L. First generation eggs (F1) reproduced were counted and further exposed up to 30 μg/L of BP-3	After 14 days, plasma concentrations of testosterone (T) significantly increased in male fish. The 17-β- estradiol (E2) to T (E2/T) ratio showed significant decreases in both male and female fish during 28 day exposure; daily average egg reproduction per female was significantly reduced at 26 μg/L of BP-3; hatchability of F1 eggs was not affected	Į
BP-3 EHMC IAMC OD-PABA OCR 4-MBC	Green alga (Scenedesmus vacuolatus)	EC ₅₀	BP-3 showed 43-fold higher toxicity than theoretically predicted. BP-3 and IAMC seem to have a more specific mode of action on algal cells	Į
BMDBM EHMC OCR	Non-biting midge (<i>Chironomus riparius</i>), oligochaete (<i>Lumbriculus variegatus</i>), and snails (<i>Melanoides tuberculata</i> and <i>Potamopyrgus</i> <i>antipodarum</i>).	56 days (L. variegatus) or 28 days (Chironomus riparius, M. tuberculata, P. antipodarum) sediment test	EHMC caused a toxic effect on reproduction in both snails with lowest observed effect concentrations (LOEC) of 0.4 mg/kg (<i>Potamopyrgus</i> <i>antipodarum</i>) and 10 mg/kg (<i>Melanoides tuberculata</i>). BDMDM and OCR showed no effects on any of the tested organisms	Į
EHMC OCR BMDBM	Planktonic crustacean (Daphnia magna)	EC ₁₀ , EC ₂₅ , and EC ₅₀ EHMC up to 80.0 μg/ml; OCR and BMDBM up to 640.0 μg/ml;	EHMC, OCR, and BMDBM highly toxic at low concentration (>1 μg/ml) and resulted in immobilization higher than 25%; immobilization reached more than 90% at concentrations of 40 μg/ml; EC ₅₀ values for EHMC, OCR, and BMDBM were 2.73, 3.18, and 1.95 μg/ml, respectively, indicating that OCR had the lowest toxic effect on <i>Daphnia</i> ; reduction of toxic effects in the mixtures of the three UV-filters, caused by antagonistic action of the components	[
n-TiO2	Cyanobacterium (Anabaena variabilis)	24 h to 6 days from 0.5 to 250 mg/L	Reduced N fixation activity, growth rate, toxicity time, and dose-dependency	[

n-TiO2	Fathead minnow (Pimephales promelas)	Exposed to 2 ng/g and 10 mg/g body weight. Challenged with fish bacterial pathogens, <i>Aeromonas hydrophila</i> or <i>Edwardsiella ictaluri</i>	Fish mortality during bacterial challenge with Aeromonas hydrophila and Edwardsiella ictalurid; reduced neutrophil phagocytosis of A. hydrophila; significant histopathological alterations	Į
n-TiO2	European sea bass (Dicentrarchus labrax)	7 days, 1 mg/L	Chromosomal alteration	[
n-TiO2	Marine scallop (<i>Chlamys farreri</i>)	14 days, 1 mg/L	Elevated superoxide dismutase (SOD), catalase (CAT) activities, and malondialdehyde (MDA) contents, increased acetylcholinesterase (AChE) activities; histopathological alterations in gills and digestive gland (dysplastic and necrosis)	Į
n-TiO ₂ n- ZnO	Diatoms (Skeletonema marinoi, Thalassiosira pseudonana), green alga (Dunaniella tertiolecta), and Haptophyta alga (Isochrysis galbana)	24 and 96 h from 0.10 to 1000 μg/L	n-TiO ₂ did not affect the growing rate, n-ZnO depressed growth in all species	ſ
n-ZnO	Diatoms (Thalassiosira pseudonana, Chaetocerus gracilis, Phaedacttylum tricornutum)	72 h, from 10 to 80 mg/L	Growth stopped in <i>T. pseudonana</i> and <i>C. gracilis</i> ; growth rate inversely proportional to NP concentration in <i>P.</i> <i>tricornutum</i> ; Zn bioaccumulation killed <i>T. pseudonana</i>	ſ
n-ZnO	Diatoms (Skeletonema costatum and Thalassiosia pseudonana), crustaceans (Tigriopus japonicus and Elasmopus rapax), and medaka fish (Oryzias melastigma)	IC ₅₀	n-ZnO toxic towards algae; ZnO toxic towards crustaceans; up-regulation of SOD and MT. Toxicity attributed mainly to dissolved Zn ions	ſ
n-ZnO	Green alga (<i>Dunaliella</i> <i>tertiolecta</i>), bioluminescent bacterium (<i>Vibrio fischeri</i>), brine shrimp (<i>Artemia salina</i>)	<i>V. fischeri</i> bioluminescence test for 5, to 30 min from 0.3 to 40 mg/L; <i>D. tertiolecta</i> algal growth test 24, 48 and 72 h from 0.1 to 10 mg/L; <i>A. salina</i> acute toxicity at 24–96 h from 10 to 100 mg/L, <i>A. salina</i> chronic exposure for 14 days from 0.03 to 0.5 mg/L	ZnO 14-day chronic exposure of <i>A</i> . salina significant inhibition of vitality and body length (EC ₅₀ 14d 0.02 mg Zn/L). ZnO NPs were more toxic towards algae (EC ₅₀ 2.2 mg Zn/L), but relatively less toxic towards bacteria (EC ₅₀ 17 mg Zn/L) and crustaceans (EC ₅₀ 96 h 58 mg Zn/L)	ť
OD-PABA OCR	Haptophyta alga (<i>Isochrysis</i> <i>galbana</i>), Mediterranean mussel (<i>Mytilus</i> <i>galloprovincialis</i>), and sea urchin (<i>Paracentrotus lividus</i>) in early stage	<i>I. galbana</i> 72 h to 2 and 90 ng/L, <i>M. galloprovinciali</i> s and <i>P. lividu</i> s 48 h EC ₅₀	OCR was the more toxic compound for <i>P. lividus</i> ; OD-PABA caused a severe negative effect on both <i>M.</i> galloprovincialis and <i>I. galbana</i>	[

n-TiO ₂	Mediterranean mussel (<i>Mytilus</i> galloprovincialis)	96 h from 1 to 100 μg/L	Lysosomal and oxidative stress; decreased transcription of antioxidant and immune-related genes; decreased lysosomal membrane stability and phagocytosis; increased oxyradical production and transcription of antimicrobial peptides; pre-apoptotic processes
Sunscreen containing BP-3, sunscreen containing TiO ₂	Clownfish (Amphiprion ocellaris)	97 h from 0 mg/L, 1 mg/L, 3 mg/L, 10 mg/L, 30 mg/L and 100 mg/L	Exposure level of 100 mg/L of BP-3 containing sunscreen led to 25% death and 100% disrupted swimming behavior by the end of the 97-h testing period. 100% of the animals failed to feed over the first 49 h of testing TiO ₂ sunscreen at 100 mg/L had 6.7% mortality, swimming behavior was disrupted during the first 25 h of testing (26.7% abnormal movement), animals recovered well over the remainder of the testing period (out to 97 h)
4-MBC	Japanese clam (Ruditapes philippinarum)	0, 1, 10, 100 µg/L over a 7- day period followed by a 3- day depuration period (total 10 days)	Assessed mortality reached up to 100 % at concentration of 100 μg/L. LC50 value of 7.71 μg/L-was derived
4-MBC	Copepod (<i>Tigriopus japonicus</i>)	Exposed to three different salinity conditions (20, 30, and 40 ppt) prior to exposure to 0, 1, and 5 µg/L for multiple generations (F0-F3)	Environmentally relevant concentrations of 4-MBC had toxic effects on <i>T. japonicus</i> . Higher salinity levels increased the lethal, developmental, and reproductive toxicities of 4-MBC in <i>T. japonicus</i>
BP-3 BEMT BMDBM MBBT OCS DHHB	Brine shrimp (A <i>rtemia salina</i>) and green algae (<i>Tetraselmis</i> <i>spp</i> .)	<i>A. salina</i> 48 h exposure at 0, 0.02, 0.2, 2, 20, 200, and 2000 μg/L; <i>Tetraselmis spp.</i> 7- day exposure at 10, 100, and	HMS and OCR were the most toxic, followed by BMDBM, on <i>A. salina</i> at high concentrations (1 mg/L). OCS, BP3 and DHHB affected metabolic activity of green algae at 100 µg/L. BEMT, DBT, EHT, and MBBT had no
DBT EHT HMS OCR		1000 μg/L	effects, even at high concentrations (2 mg/L).

Legend: benzophenone (BP) and its derivatives (2-HBP, BP-1, BP-2, BP-3, BP-4, BP-7, and BP-8); 3-benzylidene camphor (3-BC); octyl methoxycinnamate or ethylhexyl methoxycinnamate (EHMC); octocrylene (OCR); butyl methoxydibenzoylmethane or avobenzone (BMDBM); homosalate (HMS); iso-amylmethoxy-cinnamate (IAMC); 4-methylbenzylidene camphor (4-MBC); ethyl-4-aminobenzoate (Et-PABA); 2-ethylhexyl 4-dimethylaminobenzoate (OD-PABA); 2-phenylbenzimidazole-5-sulfonic acid (PBSA); bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT); methylene bis-benzotriazolyl tetramethylbutylphenol (MBBT); 2-ethylhexyl salicylate (OCS); diethylaminohydroxybenzoyl hexyl benzoate (DHHB); diethylhexyl butamido triazone (DBT); ethylhexyl triazone (EHT); nanostructured titanium dioxide (n-TiO₂); nanostructured zinc oxide (n-ZnO).

[

[

[

[

[

Samplings of wild Mytilus edulis and Mytilus galloprovincialis in ten sites along the French Atlantic and Mediterranean coasts from June to November 2008 showed accumulation of EHMC, OCR, and OD-PABA, highlighting how these concentrations significantly increased with the rising air temperature in summer and recreational pressure, although they also depended on the geomorphological structure of the sampling sites^[70]. Studies carried out in the Hong Kong coastal area showed that the occurrence of these compounds was linked to the level of anthropogenic activities^[71]. To validate patterns and the occurrence of PCPs in coastal sites impacted by recreational activities, diurnal variations (mirroring variations in recreational activities) as well as the tourist season^[72] must be taken into consideration when writing monitoring protocols. In mussels, diurnal variations in OCR were observed, with the lowest concentrations recorded in the morning and then increasing throughout the day^[24]. An alarming fact about organic UV filters is their diffusion in the planet's waters, wherein some of these compounds can be indicated as ubiquitous contaminants in the oceans: in a study conducted on marine water between the Pacific and the Atlantic Ocean and the Arctic Sea noted the presence, in each sample, of four UV filters (BP-3, OCR, BMDBM, and EHMC). The least polluted samples of the 12 organic UV filters tested were those of Shantou and Chaozhou (5 OUVs each), two cities in southern China near the mouth of the Han river, while the most polluted ones came from Hong Kong, in whose waters all 12 of the compounds analyzed were found^[21]. Organic UV filters were reported as present in Arctic waters, far away from anthropogenic sources, and it's been hypothesized that these molecules were transported there by major oceanic currents from the conveyor belt^[21].

The benthic community seems to be the most impacted by the presence of PCPs, since hydrophobic UV filters accumulate in the sediment phase^[22], but the presence of UV filters may also enhance the spread of viral infection on both benthic and pelagic organisms^[11]. At present, studies performed on the general formula or with a combination of UV filters are scarce both for the human body^[73] and the environment^[14]. Moreover, some organic UV filters seem to have estrogenic effects, but their activity and interactions in mixtures are largely unknown^{[51][74]}. In particular, laboratory studies seemed to show that BP-3 showed anti-androgenic activities in zebrafish (*Danio rerio*) and Japanese medaka (*Oryzias latipes*)^{[52][53]}.

The analysis of biological tissues is used to identify bioaccumulation or biomagnification of organic UV filters along the food chain. Organic UV filters seem to accumulate with patterns similar to PCBs, highly persistent pollutants^[Z5], with the potential to reach marine mammals^[Z6]. In a laboratory experiment performed on swamp crayfish (*Procambarus clarkii*), five organic UV filters (BP-3, 4-MBC, OCR, EHMC, and HMS) were tested for bioaccumulation and both 4-MBC and OCR showed accumulation in fecal matter, while EHMC and HMS showed the highest bioaccumulation factors^[Z2]. In a natural environment, the presence of organic UV filters was ubiquitous in Lebranche mullet (*Mugil liza*) samples taken in the highly urbanized Guanabara Bay (Rio de Janeiro, Brazil) and data suggested an estimated daily intake in humans, via diet, from 0.3 to 15.2 ng of UV filters (kg/body weight). Therefore, UV filters might pose a hazard to human health as well^[Z8]. To date, few data are available regarding the bioaccumulation and biomagnification processes, even if bioaccumulation has been detected^{[24][79]}. This suggests that further evaluation must be undertaken to gain knowledge on the fate of these compounds along the trophic chain.

4. Toxicity on Coral Reef

Barrier reefs are unique ecosystems that, in recent years, have been threatened by increasingly frequent bleaching events. A bleaching event refers to the loss of symbiotic zooxanthellae hosted within scleractinian corals, often causing the death of the whole coral and therefore a loss of biodiversity in the ecosystem. It is thought that up to 10% of all coral reefs on the planet are menaced by these events^[11]. Latent infections are common in symbiotic zooxanthellans^[80], but a link was established between the weakening of coral due to exposition to sunscreen and the occurrence of viral infections, suggesting that the presence of PCPs, especially BP-3 and BP-8, could be a joint cause^{[11][80][81]}. For example, BP-3 exceeded the threshold values by over 20% in hard corals (Acropora sp. and A. pulchra) in Hong Kong beaches located near snorkeling spots. It should be noted that these two compounds were detected widely and frequently at high concentrations in most of the sampled locations, causing larval deformity and mortality^[82]. BP-3 is so far a ubiquitous presence in coastal seawater, sediment, and coral tissue, as also determined from sampling at sites around Oahu, Hawaii^[83]. Taking into consideration the official data of the UNWTO, it was evaluated that 10% of the total sunscreen used is used in barrier reef tropical areas, and these data raise consistent concerns for the conservation of these endangered environments. Even so, relatively few studies have been conducted to identify environmental concentrations and potential toxicity of organic and inorganic UV filters[11][21][32][83][84]. Overall, there is a strong need to improve our understanding of the in situ concentrations of UV filters and preservatives, as well as their individual and combined effects. The environmentally measured concentrations are generally significantly lower than the nominal concentrations used in the laboratory to assess toxicity, but co-effects with other parameters may be crucial to assess risks for these compounds. Recently, it was discovered that mostly organic filters, such as BP-3, showed exacerbated adverse effects in the light[BS], confirming that the concentration itself may not be the only parameter to consider. The assessment of risk should include biotic parameters (e.g., sensitivities, life stages of coral, metabolic capacities focus on both the host and symbionts) as well as abiotic parameters (e.g., solar irradiation, presence of other pollutants, and water temperature). Furthermore, adult corals were proven to accumulate and metabolize BPs during exposure in laboratory^[81], but these effects have not yet been fully evaluated.

Concerning inorganic UV filters, uncoated ZnO induced severe bleaching and stimulated a microbial enrichment in the seawater that surrounds the corals^[86]. Moreover, the maximum photosynthetic efficiency (Fv/Fm) of symbiotic zooxanthellae in scleractinian coral (*Stylophora pistillata*) when exposed to 90 μ g/L of ZnO for 35 days, was reduced by 38% as compared to the control^[87]. This clearly shows that ZnO is not an environmentally friendly compound and that its impact should be carefully evaluated.

In contrast, TiO_2 coated with alumina and dimethicone and TiO_2 modified with manganese caused minimal alterations in symbiotic interactions and did not cause bleaching, thus making it more eco-friendly than $ZnO^{[\underline{86}]}$. Alongside the direct impact on corals, UV filters also seem to pose a significant threat to reef biota, suggesting population and colony decline, as well as behavioral changes, for some common inhabitants of the reefs^{[11][32]}.

The studies taken into consideration are synthesized in Table 2.

Table 2. Effects of various UV filters on corals and reef biota.

UV filter(s)	Organism(s)	Exposure conditions	Effects	Reference
ZnO	Acropora spp. coral nubbins	24 and 48 h, up to 6.3 mg/L	67% coral nubbins surface bleached	[<u>86]</u>
BMDBM 2% BP-3 6% EHMC 6% OCR 6% OCS 5% 4-MBC 3% Butylparaben 0.5% and commercial sunscreens	Acropora spp. coral nubbins, Stylophora pistillata and Millepora complanata	18, 48 and 96 h, final concentrations of 10, 33, 50, and 100 μL/L	Sunscreen even in very low quantities (i.e., 10 μL/L) resulted in the release of large amounts of coral mucus (composed of zoo- xanthellae and coral tissue) within 18–48 h and complete bleaching of hard corals within 96 h	[11]
BP-3	Stylophora pistillata (larval form)	PB-3 EC ₅₀ and LC ₅₀ , with different light exposure (8 h in the light, 8 h in the dark, a full diurnal cycle of 24 h, beginning at 08:00 in daylight and darkness from 18:00 in the evening until 08:00 h the next day, and a full 24 h in darkness), at 0.00001, 0.0001, 0.001, 0.01, 0.1 and 1 mM	BP-3 transformed planulae from a motile state to a deformed and sessile condition, showing genotoxicant, skeletal, and endocrine disruptor activity. BP-3 effects exacerbated in the light	[85]

ZnO Ethylparaben Butylparaben TDSA DTS EHT BMDBM OCR	Stylophora pistillata	35 days: ZnO from 10 to 1000 μg/L, UV filters from 10 to 5000 μg/L, preservatives (Ethylparaben and Butylparaben) from 0.1 a 1000 μg/L	ZnO reduced photosynthetic efficiency Fv/Fm by 38%, no adverse effects on the other UV filters tested up to the concentration corresponding to their water solubility limit. Butylparaben decreased the Fv/Fm by 25% at the highest concentration of 100 µg/L	[<u>87]</u>
BP-1 BP-3 BP-4 BP-8	Pocillopora damicornis, Seriatopora caliendrum	7-12 days from 0.1 to 1000 μg/L. <1000 μg/L (S. <i>caliendrum</i> nubbins)	No bleaching was observed in the <i>P</i> . damicornis larval tests, while bleaching was observed in the <i>P</i> . damicornis nubbin tests. Overall, BP-1 and BP-8 were more toxic to the two tested species than BP-3 and BP-4, which matches the relative bioaccumulation potential of the four BPs (BP-8 > BP-1 \approx BP-3 > BP-4)	[<u>81]</u>
HMS 13% BP-3 6% OCR 5% OCS 5% BMDBM 3%	Flatworm (<i>Convolutriloba</i> <i>macropyga</i>); pulse corals (<i>Xenia sp.</i>); glass anemones (<i>Aiptasia spp.</i>); Diatoms (<i>Nitzschia</i> <i>spp.</i>)	Flatworms: 72 h from 0.1 to 1 ml/L; pulse corals: 72 h, 1 mL in 3.8 L seawater; glass anemones: 7 days from 0.1 to 1 ml/L; diatoms: 72 h 1 ml on 3.8 L seawater	Flatworm populations exposed to sunscreen showed a highly reduced growing rate. Pulse corals showed effects on growing rate, with a drastic decrease during the first week of treatment and partially recovering in the following period, and polyp pulses per minute, slowed down after about 10 minutes of exposition. All anemones exposed to sunscreen were categorized as unhealthy since pedal disks were weakly or not attached to the container walls, tentacles or body columns were not extended, individuals did not clearly respond to touch and appeared dark brown to black. Diatoms were less green with the average green fluorescent content showing a decrease	[32]
BP-3 HMS OCS OCR	Concentrations in water, sediment, and coral tissue (Ka'a'awa, Waikiki Beach, Kaneohe Bay in October 2017)		Total mass concentrations of all UV- filters detected in seawater were < 750 ng/L, in sediment < 70 ng/g and in coral tissue < 995 ng/g dry weight (dw). UV-filter concentrations generally varied as follows: Water: HMS > OCS > BP-3 > OCR, concentrations in surface seawater highest at Waikiki beach; Sediment: HMS > OCS > OCR > BP- 3; Coral: OCS ≈ HMS > OCR ≈ BP-3	[83]

Legend: benzophenone derivatives (BP-1, BP-3, BP-4, BP-8); octyl methoxycinnamate or ethylhexyl methoxycinnamate (EHMC); octocrylene (OCR); butyl methoxydibenzoylmethane or avobenzone (BMDBM); homosalate (HMS); 4-methylbenzyliden camphor (4-MBC); micrometric zinc oxide (ZnO); ethylhexyl triazone (EHT); terephthalylidene

dicamphor sulfonic acid (TDSA); drometrizole trisiloxane (DTS); 2-ethylhexyl 2-cyano-3,3- diphenylacrylate (EHCDA); 2ethylhexyl salycilate (OCS).

5. Conclusions

Although a significant development was reached by global research on the impact of sunscreens and other photoprotective PCPs in nature, much more needs to be understood through future and more in-depth studies. The fields to be explored are many, given the recent interest in this area of environmental toxicology: while studies on nanoparticles in the Mediterranean and on organic UV filters in tropical countries are relatively abundant, ecotoxicological investigations on the average toxicity thresholds are deficient. When assessing the effects on natural coastal environments and coastal biota, we need to take into consideration parameters such as variation in pH, salinity, solar irradiation, level of anthropogenic activities, and currents etc. For example, increasing salinity levels posed a significant risk for the marine copepod *Tigropus japonicus* in the presence of different concentrations of 4-MBC by exacerbating oxidative stress and the uptake of this chemical^[69]. A special focus must be taken to monitor these compounds in natural environments and to evaluate their co-existence in shallow waters as the combination of UV filters and co-formulants may enhance or alter the toxic effects of each component. On this matter, a worldwide protocol should be created to make data easily comparable. Important gaps are also related to research on bioaccumulation and biomagnification, of both organic and inorganic UV filters, towards the trophic levels of marine ecological networks.

These new pieces of information will be necessary to improve and integrate the knowledge we have about the environmental effects of sunscreens and allow us to correct our actions and to start empowering institutions and the global population towards a greater respect for the environment. It should be added that, in recent years, we have also seen the first steps in this direction by some tropical countries that care about the fate of the coral reefs along their coasts. For example, the American State of Hawaii applied important restrictions to the ingredients of sunscreen products that can be marketed within their territory to counteract the phenomena of coral bleaching. Moreover, in this case, correct information must be made available to dissuade people from using sunscreens with banned chemicals purchased outside of the State and to reduce misunderstandings on the correct use of sunscreen^[88]. Furthermore, special attention needs to be given on Marine Protected Areas^[72].

New conservation strategies are needed to drastically reduce the impact on ecosystems^[B9], possibly developed according to the most vulnerable habitats (e.g., tropical atolls, coral reefs, the Mediterranean coral reef, and other biodiversity hotspots).

Environmental issues are becoming more recognized due to the increasing media coverage provided in this regard, but comprehensive knowledge is lacking. Future legislation for a "coral safe" labelling might be addressed to help people make informed purchases^[90]. By pushing this, initiatives could be promoted to decrease individual impacts on the environment with small gestures that can make a big difference when adopted by many people. For example, reducing the surface of application and the use of opaque garments, such as one-piece swimsuits instead of two-piece swimsuits. The research on new photoprotective compounds, extracted directly from plants, algae and animals, should be encouraged to identify sustainable molecules, easily degradable by organisms. This could be a promising development sector for research institutions and industries working towards a more sustainable future.

References

- 1. UNEP Sustainable Coastal Tourism An integrated planning and management approach. UNEP. Retrieved 2021-8-18
- 2. UNDP Sustainable Development Goals. Goal 14: Life Below Water . UNDP. Retrieved 2021-8-18
- David Sánchez-Quiles; Antonio Tovar-Sánchez; Are sunscreens a new environmental risk associated with coastal touri sm?. Environment International 2015, 83, 158-170, <u>10.1016/j.envint.2015.06.007</u>.
- Antonio Tovar-Sánchez; David Sánchez-Quiles; Gotzon Basterretxea; Juan Luis Benedé; Alberto Chisvert; Amparo Sal vador; Ignacio Moreno-Garrido; Julian Blasco; Sunscreen Products as Emerging Pollutants to Coastal Waters. *PLoS O NE* 2013, 8, e65451, <u>10.1371/journal.pone.0065451</u>.
- 5. Dimosthenis L. Giokas; Amparo Salvador; Alberto Chisvert; UV filters: From sunscreens to human body and the enviro nment. *TrAC Trends in Analytical Chemistry* **2007**, *26*, 360-374, <u>10.1016/j.trac.2007.02.012</u>.
- Marianne E. Balmer; Hans-Rudolf Buser; Markus D. Müller; Thomas Poiger; Occurrence of Some Organic UV Filters in Wastewater, in Surface Waters, and in Fish from Swiss Lakes. *Environmental Science & Technology* 2005, *39*, 953-96 2, <u>10.1021/es040055r</u>.
- Helmieh Amine; Elena Gomez; Jalal Halwani; Claude Casellas; Hélène Fenet; UV filters, ethylhexyl methoxycinnamate, octocrylene and ethylhexyl dimethyl PABA from untreated wastewater in sediment from eastern Mediterranean river tra nsition and coastal zones. *Marine Pollution Bulletin* 2012, 64, 2435-2442, <u>10.1016/j.marpolbul.2012.07.051</u>.
- Samantha L. Schneider; Henry W. Lim; Review of environmental effects of oxybenzone and other sunscreen active ingr edients. *Journal of the American Academy of Dermatology* 2018, 80, 266-271, <u>10.1016/j.jaad.2018.06.033</u>.

- Hans-Rudolf Buser; Marianne Balmer; Peter Schmid; Martin Kohler; Occurrence of UV Filters 4-Methylbenzylidene Ca mphor and Octocrylene in Fish from Various Swiss Rivers with Inputs from Wastewater Treatment Plants. *Environment* al Science & Technology 2006, 40, 1427-1431, <u>10.1021/es052088s</u>.
- Sara Ramos; Vera Homem; Arminda Alves; Lúcia Santos; Advances in analytical methods and occurrence of organic U V-filters in the environment — A review. Science of The Total Environment 2015, 526, 278-311, <u>10.1016/j.scitotenv.201</u> <u>5.04.055</u>.
- Roberto Danovaro; Lucia Bongiorni; Cinzia Corinaldesi; Donato Giovannelli; Elisabetta Damiani; Paola Astolfi; Lucedio Greci; Antonio Pusceddu; Sunscreens Cause Coral Bleaching by Promoting Viral Infections. *Environmental Health Per* spectives 2008, 116, 441-447, 10.1289/ehp.10966.
- 12. Jérôme Labille; Danielle Slomberg; Riccardo Catalano; Samuel Robert; Marie-Laure Apers-Tremelo; Jean-Luc Bouden ne; Tarek Manasfi; Olivier Radakovitch; Assessing UV filter inputs into beach waters during recreational activity: A field study of three French Mediterranean beaches from consumer survey to water analysis. *Science of The Total Environm ent* **2019**, *706*, 136010, <u>10.1016/j.scitotenv.2019.136010</u>.
- Marinella Farre; Sandra Pérez; Lina Kantiani; Damià Barceló; Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. *TrAC Trends in Analytical Chemistry* 2008, 27, 991-1007, <u>10.1</u> 016/j.trac.2008.09.010.
- M. Sendra; David Sánchez-Quiles; Julian Blasco; Ignacio Moreno-Garrido; L.M. Lubián; S. Pérez-García; A. Tovar-Sán chez; Effects of TiO2 nanoparticles and sunscreens on coastal marine microalgae: Ultraviolet radiation is key variable f or toxicity assessment. *Environment International* 2017, 98, 62-68, <u>10.1016/j.envint.2016.09.024</u>.
- 15. Valeria Matranga; Ilaria Corsi; Toxic effects of engineered nanoparticles in the marine environment: Model organisms a nd molecular approaches. *Marine Environmental Research* **2012**, *76*, 32-40, <u>10.1016/j.marenvres.2012.01.006</u>.
- European Council Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products (Text with EEA relevance). OJ L 342; 2009; pp. 59–209
- 17. David Sánchez-Quiles; Antonio Tovar-Sánchez; Sunscreens as a Source of Hydrogen Peroxide Production in Coastal Waters. *Environmental Science & Technology* **2014**, *48*, 9037-9042, <u>10.1021/es5020696</u>.
- Soyoung Baek; Sung Hee Joo; Patricia Blackwelder; Michal Toborek; Effects of coating materials on antibacterial prope rties of industrial and sunscreen-derived titanium-dioxide nanoparticles on Escherichia coli. *Chemosphere* 2018, 208, 1 96-206, <u>10.1016/j.chemosphere.2018.05.167</u>.
- Céline Botta; Jérôme Labille; Mélanie Auffan; Daniel Borschneck; Hélène Miche; Martiane Cabié; Armand Masion; Jérô me Rose; Jean-Yves Bottero; TiO2-based nanoparticles released in water from commercialized sunscreens in a life-cyc le perspective: Structures and quantities. *Environmental Pollution* **2011**, *159*, 1543-1550, <u>10.1016/j.envpol.2011.03.00</u>
 <u>3</u>.
- 20. Mélanie Auffan; Maxime Pedeutour; Jérôme Rose; Armand Masion; Fabio Ziarelli; Daniel Borschneck; Corinne Chanea c; Céline Botta; Perrine Chaurand; Jérôme Labille; et al. Structural Degradation at the Surface of a TiO2-Based Nanom aterial Used in Cosmetics. *Environmental Science & Technology* **2010**, *44*, 2689-2694, <u>10.1021/es903757q</u>.
- 21. Mirabelle M.P. Tsui; H.W. Leung; Tak-Cheung Wai; Nobuyoshi Yamashita; Sachi Taniyasu; Wenhua Liu; Kwan Sing Pau I Lam; Margaret B. Murphy; Occurrence, distribution and ecological risk assessment of multiple classes of UV filters in surface waters from different countries. *Water Research* **2014**, *67*, 55-65, <u>10.1016/j.watres.2014.09.013</u>.
- 22. S. K. Fagervold; A. S. Rodrigues; C. Rohée; R. Roe; M. Bourrain; Didier Stien; P. LeBaron; Occurrence and Environme ntal Distribution of 5 UV Filters During the Summer Season in Different Water Bodies. *Water, Air, & Soil Pollution* 2019, 230, 172, 10.1007/s11270-019-4217-7.
- Binni Ma; Guanghua Lu; Fuli Liu; Yang Nie; Zhenghua Zhang; Yi Li; Organic UV Filters in the Surface Water of Nanjing, China: Occurrence, Distribution and Ecological Risk Assessment. *Bulletin of Environmental Contamination and Toxicol* ogy 2016, 96, 530-535, <u>10.1007/s00128-015-1725-z</u>.
- Marina Picot-Groz; Hélène Fenet; María Jesus Martínez Bueno; David Rosain; Elena Gomez; Diurnal variations in pers onal care products in seawater and mussels at three Mediterranean coastal sites. *Environmental Science and Pollution Research* 2018, 25, 9051-9059, <u>10.1007/s11356-017-1100-1</u>.
- Antonio Tovar-Sánchez; Erica Sparaventi; Amandine Gaudron; Araceli Rodríguez-Romero; A new approach for the dete rmination of sunscreen levels in seawater by ultraviolet absorption spectrophotometry. *PLOS ONE* 2020, 15, e024359 1, 10.1371/journal.pone.0243591.
- 26. Anja Engel; Hermann W. Bange; Michael Cunliffe; Susannah M. Burrows; Gernot Friedrichs; Luisa Galgani; Hartmut H errmann; Norbert Hertkorn; Martin Johnson; Peter S. Liss; et al. The Ocean's Vital Skin: Toward an Integrated Understa nding of the Sea Surface Microlayer. *Frontiers in Marine Science* **2017**, *4*, 1-14, <u>10.3389/fmars.2017.00165</u>.
- Araceli Rodríguez-Romero; Gema Ruiz-Gutiérrez; Javier R. Viguri; Antonio Tovar-Sánchez; Sunscreens as a New Sour ce of Metals and Nutrients to Coastal Waters. *Environmental Science & Technology* 2019, 53, 10177-10187, <u>10.1021/a</u> <u>cs.est.9b02739</u>.
- Arturo A. Keller; Hongtao Wang; Dongxu Zhou; Hunter S. Lenihan; Gary Cherr; Bradley J. Cardinale; Robert Miller; Zha oxia Ji; Stability and Aggregation of Metal Oxide Nanoparticles in Natural Aqueous Matrices. *Environmental Science & Technology* 2010, 44, 1962-1967, <u>10.1021/es902987d</u>.

- 29. Beng Joo Reginald Thio; Dongxu Zhou; Arturo A. Keller; Influence of natural organic matter on the aggregation and dep osition of titanium dioxide nanoparticles. *Journal of Hazardous Materials* **2011**, *18*9, 556-563, <u>10.1016/j.jhazmat.2011.0</u> <u>2.072</u>.
- Zuzanna A. Lewicka; William W. Yu; Brittany L. Oliva; Elizabeth Quevedo Contreras; Vicki L. Colvin; Photochemical be havior of nanoscale TiO2 and ZnO sunscreen ingredients. *Journal of Photochemistry and Photobiology A: Chemistry* 2 013, 263, 24-33, 10.1016/j.jphotochem.2013.04.019.
- 31. Yuanyuan Li; Dongjie Yang; Shuo Lu; Xueqing Qiu; Yong Qian; Pengwei Li; Encapsulating TiO2 in Lignin-Based Colloid al Spheres for High Sunscreen Performance and Weak Photocatalytic Activity. *ACS Sustainable Chemistry & Engineeri ng* **2019**, *7*, 6234-6242, <u>10.1021/acssuschemeng.8b06607</u>.
- Shaun M. McCoshum; Alicia M. Schlarb; Kristen Baum; Direct and indirect effects of sunscreen exposure for reef biota. *Hydrobiologia* 2016, 776, 139-146, <u>10.1007/s10750-016-2746-2</u>.
- John M. Allen; Cynthia J. Gossett; Sandra K. Allen; Photochemical Formation of Singlet Molecular Oxygen in Illuminate d Aqueous Solutions of Several Commercially Available Sunscreen Active Ingredients. *Chemical Research in Toxicolog* y 1996, 9, 605-609, <u>10.1021/tx950197m</u>.
- J. Johnson Inbaraj; Piotr Bilski; Colin F. Chignell; Photophysical and Photochemical Studies of 2-Phenylbenzimidazole and UVB Sunscreen 2-Phenylbenzimidazole-5-sulfonic Acid¶. *Photochemistry and Photobiology* 2002, 75, 107-16, <u>10.</u> <u>1562/0031-8655(2002)075<0107:papsop>2.0.co;2</u>.
- 35. F. M. M. Morel; The Biogeochemical Cycles of Trace Metals in the Oceans. *Science* **2003**, *300*, 944-947, <u>10.1126/scien</u> <u>ce.1083545</u>.
- 36. Kristina Kotnik; Tina Kosjek; Bojana Žegura; Metka Filipič; Ester Heath; Photolytic fate and genotoxicity of benzopheno ne-derived compounds and their photodegradation mixtures in the aqueous environment. *Chemosphere* 2016, 147, 11 4-123, 10.1016/j.chemosphere.2015.12.068.
- Rosario Rodil; Monika Moeder; Rolf Altenburger; Mechthild Schmitt-Jansen; Photostability and phytotoxicity of selected sunscreen agents and their degradation mixtures in water. *Analytical and Bioanalytical Chemistry* 2009, 395, 1513-152 4, 10.1007/s00216-009-3113-1.
- Laura A. MacManus-Spencer; Monica L. Tse; Jacob L. Klein; Alison E. Kracunas; Aqueous Photolysis of the Organic UI traviolet Filter Chemical Octyl Methoxycinnamate. *Environmental Science & Technology* 2011, 45, 3931-3937, <u>10.1021/</u> <u>es103682a</u>.
- 39. E. Paredes; S. Perez; Rosario Rodil; José Benito Quintana; Ricardo Beiras; Ecotoxicological evaluation of four UV filter s using marine organisms from different trophic levels Isochrysis galbana, Mytilus galloprovincialis, Paracentrotus lividu s, and Siriella armata. *Chemosphere* 2014, 104, 44-50, <u>10.1016/j.chemosphere.2013.10.053</u>.
- L. Canesi; R. Fabbri; G. Gallo; D. Vallotto; A. Marcomini; G. Pojana; Biomarkers in Mytilus galloprovincialis exposed to suspensions of selected nanoparticles (Nano carbon black, C60 fullerene, Nano-TiO2, Nano-SiO2). *Aquatic Toxicology* 2010, 100, 168-177, <u>10.1016/j.aquatox.2010.04.009</u>.
- Antoni Sureda; Xavier Capó; Carla Busquets-Cortés; Silvia Tejada; Acute exposure to sunscreen containing titanium in duces an adaptive response and oxidative stress in Mytillus galloprovincialis. *Ecotoxicology and Environmental Safety* 2018, 149, 58-63, <u>10.1016/j.ecoenv.2017.11.014</u>.
- 42. Xiaoshan Zhu; Jin Zhou; Zhonghua Cai; The toxicity and oxidative stress of TiO2 nanoparticles in marine abalone (Hali otis diversicolor supertexta). *Marine Pollution Bulletin* **2011**, *63*, 334-338, <u>10.1016/j.marpolbul.2011.03.006</u>.
- Tamara Galloway; Ceri Lewis; Ida Dolciotti; Blair D. Johnston; Julian Moger; Francesco Regoli; Sublethal toxicity of nan o-titanium dioxide and carbon nanotubes in a sediment dwelling marine polychaete. *Environmental Pollution* 2010, 158, 1748-1755, <u>10.1016/j.envpol.2009.11.013</u>.
- Sonia Manzo; Simona Schiavo; Maria Oliviero; Alfonso Toscano; Martina Ciaravolo; Paola Cirino; Immune and reprodu ctive system impairment in adult sea urchin exposed to nanosized ZnO via food. *Science of The Total Environment* 201 7, 599-600, 9-13, <u>10.1016/j.scitotenv.2017.04.173</u>.
- M.J. Araújo; Rui Rocha; A.M.V.M. Soares; J.L. Benedé; A. Chisvert; Marta Monteiro; Effects of UV filter 4-methylbenzyli dene camphor during early development of Solea senegalensis Kaup, 1858. Science of The Total Environment 2018, 6 28-629, 1395-1404, 10.1016/j.scitotenv.2018.02.112.
- 46. Hui Liu; Ping Sun; Hongxia Liu; Shaogui Yang; Liansheng Wang; Zunyao Wang; Acute toxicity of benzophenone-type U V filters for Photobacterium phosphoreum and Daphnia magna: QSAR analysis, interspecies relationship and integrate d assessment. *Chemosphere* **2015**, *135*, 182-188, <u>10.1016/j.chemosphere.2015.04.036</u>.
- 47. Katerina Grabicova; Ganna Fedorova; Viktoriia Burkina; Christoph Steinbach; Heike Schmidt-Posthaus; Vladimír Žlábe k; Hana Kroupova; Roman Grabic; Tomas Randak; Presence of UV filters in surface water and the effects of phenylben zimidazole sulfonic acid on rainbow trout (Oncorhynchus mykiss) following a chronic toxicity test. *Ecotoxicology and En vironmental Safety* **2013**, *96*, 41-47, <u>10.1016/j.ecoenv.2013.06.022</u>.
- 48. Li Gao; Tao Yuan; Peng Cheng; Chuanqi Zhou; Junjie Ao; Wenhua Wang; Haimou Zhang; Organic UV filters inhibit mul tixenobiotic resistance (MXR) activity in Tetrahymena thermophila: investigations by the Rhodamine 123 accumulation assay and molecular docking. *Ecotoxicology* **2016**, *25*, 1318-1326, <u>10.1007/s10646-016-1684-0</u>.

- Qiuya Zhang; Xiaoyan Ma; Mawuli Dzakpasu; Xiaochang C. Wang; Evaluation of ecotoxicological effects of benzophen one UV filters: Luminescent bacteria toxicity, genotoxicity and hormonal activity. *Ecotoxicology and Environmental Safe* ty 2017, 142, 338-347, 10.1016/j.ecoenv.2017.04.027.
- 50. Feijian Mao; Yiliang He; Karina Yew-Hoong Gin; Evaluating the Joint Toxicity of Two Benzophenone-Type UV Filters on the Green Alga Chlamydomonas reinhardtii with Response Surface Methodology. *Toxics* **2018**, *6*, 8, <u>10.3390/toxics601</u> <u>0008</u>.
- 51. Karl Fent; Petra Kunz; Elena Gomez; UV Filters in the Aquatic Environment Induce Hormonal Effects and Affect Fertility and Reproduction in Fish. *CHIMIA International Journal for Chemistry* **2008**, *62*, 368-375, <u>10.2533/chimia.2008.368</u>.
- 52. Nancy Blüthgen; Sara Zucchi; Karl Fent; Effects of the UV filter benzophenone-3 (oxybenzone) at low concentrations in zebrafish (Danio rerio). *Toxicology and Applied Pharmacology* **2012**, *263*, 184-194, <u>10.1016/j.taap.2012.06.008</u>.
- 53. Sujin Kim; Dawoon Jung; Younglim Kho; Kyungho Choi; Effects of benzophenone-3 exposure on endocrine disruption and reproduction of Japanese medaka (Oryzias latipes)—A two generation exposure study. *Aquatic Toxicology* **2014**, *1* 55, 244-252, <u>10.1016/j.aquatox.2014.07.004</u>.
- D. Kaiser; A. Sieratowicz; H. Zielke; M. Oetken; H. Hollert; Jörg Oehlmann; Ecotoxicological effect characterisation of w idely used organic UV filters. *Environmental Pollution* 2012, 163, 84-90, <u>10.1016/j.envpol.2011.12.014</u>.
- 55. Chang-Beom Park; Jiyi Jang; Sanghun Kim; Young Jun Kim; Single- and mixture toxicity of three organic UV-filters, eth ylhexyl methoxycinnamate, octocrylene, and avobenzone on Daphnia magna. *Ecotoxicology and Environmental Safety* 2017, 137, 57-63, <u>10.1016/j.ecoenv.2016.11.017</u>.
- 56. Carla Cherchi; April Z. Gu; Impact of Titanium Dioxide Nanomaterials on Nitrogen Fixation Rate and Intracellular Nitrog en Storage inAnabaena variabilis. *Environmental Science & Technology* **2010**, *44*, 8302-8307, <u>10.1021/es101658p</u>.
- Boris Jovanović; Elizabeth M. Whitley; Kayoko Kimura; Adam Crumpton; Dušan Palić; Titanium dioxide nanoparticles e nhance mortality of fish exposed to bacterial pathogens. *Environmental Pollution* 2015, 203, 153-164, <u>10.1016/j.envpol.</u> 2015.04.003.
- 58. M. Nigro; M. Bernardeschi; Domenico Costagliola; C. Della Torre; G. Frenzilli; P. Guidi; P. Lucchesi; F. Mottola; M. Sant onastaso; V. Scarcelli; et al. n-TiO2 and CdCl2 co-exposure to titanium dioxide nanoparticles and cadmium: Genomic, DNA and chromosomal damage evaluation in the marine fish European sea bass (Dicentrarchus labrax). *Aquatic Toxic ology* **2015**, *168*, 72-77, <u>10.1016/j.aquatox.2015.09.013</u>.
- Bin Xia; Lin Zhu; Qian Han; Xuemei Sun; Bijuan Chen; Keming Qu; Effects of TiO 2 nanoparticles at predicted environ mental relevant concentration on the marine scallop Chlamys farreri : An integrated biomarker approach. *Environmenta I Toxicology and Pharmacology* 2017, 50, 128-135, <u>10.1016/j.etap.2017.01.016</u>.
- Robert J. Miller; Hunter S. Lenihan; Erik Muller; Nancy Tseng; Shannon K. Hanna; Arturo A. Keller; Impacts of Metal Ox ide Nanoparticles on Marine Phytoplankton. *Environmental Science & Technology* 2010, 44, 7329-7334, <u>10.1021/es10</u> 0247x.
- 61. Xiaohui Peng; Shelagh Palma; Nicholas S. Fisher; Stanislaus S. Wong; Effect of morphology of ZnO nanostructures on their toxicity to marine algae. *Aquatic Toxicology* **2011**, *102*, 186-196, <u>10.1016/j.aquatox.2011.01.014</u>.
- Stella W. Y. Wong; Priscilla T. Y. Leung; A. B. Djurišić; Kenneth Mei Yee Leung; Toxicities of nano zinc oxide to five mari ne organisms: influences of aggregate size and ion solubility. *Analytical and Bioanalytical Chemistry* 2009, 396, 609-61 8, <u>10.1007/s00216-009-3249-z</u>.
- Simona Schiavo; Maria Oliviero; Jiji Li; Sonia Manzo; Testing ZnO nanoparticle ecotoxicity: linking time variable exposu re to effects on different marine model organisms.. *Environmental Science and Pollution Research* 2017, 25, 4871-488 0, 10.1007/s11356-017-0815-3.
- A. Giraldo; Rosa Montes; Rosario Rodil; José Benito Quintana; L. Vidal-Liñán; Ricardo Beiras; Ecotoxicological Evaluat ion of the UV Filters Ethylhexyl Dimethyl p-Aminobenzoic Acid and Octocrylene Using Marine Organisms Isochrysis gal bana, Mytilus galloprovincialis and Paracentrotus lividus. *Archives of Environmental Contamination and Toxicology* 201 7, 72, 606-611, <u>10.1007/s00244-017-0399-4</u>.
- 65. Cristina Barmo; Caterina Ciacci; Barbara Canonico; Rita Fabbri; Katia Cortese; Teresa Balbi; Antonio Marcomini; Giulio Pojana; Gabriella Gallo; Laura Canesi; et al. In vivo effects of n-TiO2 on digestive gland and immune function of the ma rine bivalve Mytilus galloprovincialis. *Aquatic Toxicology* **2013**, *132-133*, 9-18, <u>10.1016/j.aquatox.2013.01.014</u>.
- Alexandra N. Barone; Caitlyn E. Hayes; James J. Kerr; Ryan C. Lee; Denise B. Flaherty; Acute toxicity testing of TiO2based vs. oxybenzone-based sunscreens on clownfish (Amphiprion ocellaris). *Environmental Science and Pollution Re* search 2019, 26, 14513-14520, <u>10.1007/s11356-019-04769-z</u>.
- 67. Melania Santonocito; Barbara Salerno; Chiara Trombini; Federico Tonini; Marina G. Pintado-Herrera; Gonzalo Martinez -Rodriguez; Julian Blasco; Pablo Antonio Lara-Martín; Miriam Hampel; Stress under the sun: Effects of exposure to low concentrations of UV-filter 4- methylbenzylidene camphor (4-MBC) in a marine bivalve filter feeder, the Manila clam Ru ditapes philippinarum. *Aquatic Toxicology* **2020**, *221*, 105418, <u>10.1016/j.aquatox.2020.105418</u>.
- Haizheng Hong; Jiaxin Wang; Dalin Shi; Effects of salinity on the chronic toxicity of 4-methylbenzylidene camphor (4-M BC) in the marine copepod Tigriopus japonicus. *Aquatic Toxicology* 2021, 232, 105742, <u>10.1016/j.aquatox.2021.10574</u>
 <u>2</u>.

- 69. Evane Thorel; Fanny Clergeaud; Lucie Jaugeon; Alice M. S. Rodrigues; Julie Lucas; Didier Stien; Philippe LeBaron; Eff ect of 10 UV Filters on the Brine Shrimp Artemia salina and the Marine Microalga Tetraselmis sp.. *Toxics* **2020**, *8*, 29, <u>1</u> 0.3390/toxics8020029.
- Morgane Bachelot; Zhi Li; Dominique Munaron; Patrik Le Gall; Claude Casellas; Hélène Fenet; Elena Gomez; Organic UV filter concentrations in marine mussels from French coastal regions. *Science of The Total Environment* 2012, 420, 2 73-279, <u>10.1016/j.scitotenv.2011.12.051</u>.
- 71. Ziye Sang; Kelvin Sze-Yin Leung; Environmental occurrence and ecological risk assessment of organic UV filters in ma rine organisms from Hong Kong coastal waters. *Science of The Total Environment* **2016**, 566-567, 489-498, <u>10.1016/j.s</u> <u>citotenv.2016.05.120</u>.
- V. Moschino; M. Schintu; A. Marrucci; B. Marras; N. Nesto; L. Da Ros; An ecotoxicological approach to evaluate the eff ects of tourism impacts in the Marine Protected Area of La Maddalena (Sardinia, Italy). *Marine Pollution Bulletin* 2017, 122, 306-315, <u>10.1016/j.marpolbul.2017.06.062</u>.
- Petra Y. Kunz; Karl Fent; Estrogenic activity of UV filter mixtures. *Toxicology and Applied Pharmacology* 2006, 217, 86-99, <u>10.1016/j.taap.2006.07.014</u>.
- 74. Margarida Lorigo; Melissa Mariana; Elisa Cairrao; Photoprotection of ultraviolet-B filters: Updated review of endocrine d isrupting properties. *Steroids* **2018**, *131*, 46-58, <u>10.1016/j.steroids.2018.01.006</u>.
- 75. M. Silvia Díaz-Cruz; Marta Llorca; Damià Barceló; Organic UV filters and their photodegradates, metabolites and disinf ection by-products in the aquatic environment. *TrAC Trends in Analytical Chemistry* **2008**, *27*, 873-887, <u>10.1016/j.trac.2</u> <u>008.08.012</u>.
- 76. Pablo Gago-Ferrero; Mariana B. Alonso; Carolina Pacheco Bertozzi; Juliana Marigo; Lupércio Barbosa; Marta Cremer; Eduardo Secchi; Alexandre Azevedo; José Lailson-Brito Jr.; Joao P. M. Torres; et al. First Determination of UV Filters in Marine Mammals. Octocrylene Levels in Franciscana Dolphins. *Environmental Science & Technology* **2013**, *47*, 5619-5 625, <u>10.1021/es400675y</u>.
- 77. Ke He; Ethan Hain; Anne Timm; Lee Blaney; Bioaccumulation of estrogenic hormones and UV-filters in red swamp cray fish (Procambarus clarkii). *Science of The Total Environment* **2020**, 764, 142871, <u>10.1016/j.scitotenv.2020.142871</u>.
- 78. Daniel Molins-Delgado; Ramón Muñoz; Sylvia Nogueira; Mariana B. Alonso; João Paulo Torres; Olaf Malm; Roberta Lo urenço Ziolli; Rachel Hauser-Davis; Ethel Eljarrat; Damià Barceló; et al. Occurrence of organic UV filters and metabolit es in lebranche mullet (Mugil liza) from Brazil. *Science of The Total Environment* **2018**, *618*, 451-459, <u>10.1016/j.scitote</u> <u>nv.2017.11.033</u>.
- Armin Zenker; Hansruedi Schmutz; Karl Fent; Simultaneous trace determination of nine organic UV-absorbing compounds (UV filters) in environmental samples. *Journal of Chromatography A* 2008, 1202, 64-74, <u>10.1016/j.chroma.2008.06.</u> 041.
- R. Danovaro; M. Armeni; C. Corinaldesi; M.L. Mei; Viruses and marine pollution. *Marine Pollution Bulletin* 2003, 46, 301 -304, <u>10.1016/s0025-326x(02)00461-7</u>.
- 81. Tangtian He; Mirabelle Mei Po Tsui; Chih Jui Tan; Ka Yan Ng; Fu Wen Guo; Li Hsueh Wang; Te Hao Chen; Tung Yung Fan; Kwan Sing Paul Lam; Margaret Burkhardt Murphy; et al. Comparative toxicities of four benzophenone ultraviolet fil ters to two life stages of two coral species. *Science of The Total Environment* **2018**, 651, 2391-2399, <u>10.1016/j.scitoten v.2018.10.148</u>.
- Mirabelle M. P. Tsui; James C. W. Lam; Tsz Yan Ng; P. O. Ang; Margaret B. Murphy; Paul K. S. Lam; Occurrence, Distri bution, and Fate of Organic UV Filters in Coral Communities. *Environmental Science & Technology* 2017, 51, 4182-419 0, <u>10.1021/acs.est.6b05211</u>.
- 83. Carys L. Mitchelmore; Ke He; Michael Gonsior; Ethan Hain; Andrew Heyes; Cheryl Clark; Rick Younger; Philippe Schmi tt-Kopplin; Anna Feerick; Annaleise Conway; et al. Occurrence and distribution of UV-filters and other anthropogenic co ntaminants in coastal surface water, sediment, and coral tissue from Hawaii. *Science of The Total Environment* **2019**, 6 70, 398-410, <u>10.1016/j.scitotenv.2019.03.034</u>.
- 84. John M. Brausch; Gary M. Rand; A review of personal care products in the aquatic environment: Environmental concen trations and toxicity. *Chemosphere* **2010**, *82*, 1518-1532, <u>10.1016/j.chemosphere.2010.11.018</u>.
- 85. C. A. Downs; Esti Kramarsky-Winter; Roee Segal; John Fauth; Sean Knutson; Omri Bronstein; Frederic R. Ciner; Rina Jeger; Yona Lichtenfeld; Cheryl M. Woodley; et al. Toxicopathological Effects of the Sunscreen UV Filter, Oxybenzone (Benzophenone-3), on Coral Planulae and Cultured Primary Cells and Its Environmental Contamination in Hawaii and t he U.S. Virgin Islands. Archives of Environmental Contamination and Toxicology 2015, 70, 265-288, <u>10.1007/s00244-0</u> <u>15-0227-7</u>.
- Cinzia Corinaldesi; Francesca Marcellini; Ettore Nepote; Elisabetta Damiani; Roberto Danovaro; Impact of inorganic U V filters contained in sunscreen products on tropical stony corals (Acropora spp.). Science of The Total Environment 20 18, 637-638, 1279-1285, <u>10.1016/j.scitotenv.2018.05.108</u>.
- 87. Jean-Pierre Fel; Catherine Lacherez; Alaa Bensetra; Sakina Mezzache; Eric Beraud; Marc Léonard; Denis Allemand; C hristine Ferrier-Pagès; Photochemical response of the scleractinian coral Stylophora pistillata to some sunscreen ingre dients. *Coral Reefs* **2018**, *38*, 109-122, <u>10.1007/s00338-018-01759-4</u>.

- 88. Jay Sirois; Examine all available evidence before making decisions on sunscreen ingredient bans. *Science of The Total Environment* **2019**, 674, 211-212, <u>10.1016/j.scitotenv.2019.04.137</u>.
- Cinzia Corinaldesi; Elisabetta Damiani; Francesca Marcellini; Carla Falugi; Luca Tiano; Francesca Brugè; Roberto Dan ovaro; Sunscreen products impair the early developmental stages of the sea urchin Paracentrotus lividus. *Scientific Re ports* 2017, 7, 1-12, <u>10.1038/s41598-017-08013-x</u>.
- 90. Arielle Levine; Sunscreen use and awareness of chemical toxicity among beach goers in Hawaii prior to a ban on the s ale of sunscreens containing ingredients found to be toxic to coral reef ecosystems. *Marine Policy* 2020, 117, 103875, 10.1016/j.marpol.2020.103875.

Retrieved from https://encyclopedia.pub/entry/history/show/31068