Review

Sunscreens' UV Filters Risk for Coastal Marine Environment Biodiversity: A Review

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Abstract: 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 beach-goers in recent decades. UV filters contained in sunscreens, however, were recently identified as emerging pollutants in coastal waters since they accumulate in the marine environment with different adverse effects. In fact, exposure to these components was proven to be toxic to most invertebrate and vertebrate marine species. Some UV filters are linked to the production of significant amounts of reactive oxygen species (ROS), such as hydrogen peroxide, and the release of inorganic micronutrients that may alter the status of coastal habitats. Bioaccumulation and biomagnification have not yet been fully addressed. This review highlights recent progress in research and provides a comprehensive overview of the toxicological and ecotoxicological effects of the most used UV filters both on the abiotic and biotic compartments in different types of coastal areas, to gain a better understanding of the impacts on coastal biodiversity.

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]. In fact, in 2017, the Mediterranean sea alone attracted over 267 million international tourists [2]. 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 [3]. 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 [4–6], resulting in a direct input from swimming and bathing (non-point sources). These inputs, together with industrial wastewater discharges (point sources) [7–9], are capable of starting decay processes, irreversible at times [6]. In fact, coastal tourism is acknowledged as a source of impact on shallow-water marine habitats [1], as well as lakes and rivers [10,11]. Unfortunately, recent data about the global annual production of these PCPs are lacking. Last available data from a market study in 2005 estimated a 10,000 tons of sunscreens global production per year [12]. 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 [13]. 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 [14]. 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 [4,15–17].

1.1. Sunscreen Definition

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 [18].

1.1.1. Organic Filters

Organic filters (or *chemical*) are synthesized substances, which include the derivatives of cinnamic acid such as ethylhexyl methoxycinnamate (EHMC), benzophenones (BPs) such as the commonly used benzophenone-3 (BP-3), salicylates such as ethylhexyl salicylate (OCS), benzoyl derivatives such as diethylamino hydroxybenzoyl hexyl benzoate (DHHB), and butyl methoxydibenzoylmethane (BMDBM). These compounds usually have single or multiple aromatic structures, sometimes conjugated with carbon-carbon double bonds and carbonyl moieties, able to attenuate the transmission of energetic solar photons that reach the surface of the Earth [6]. These molecules typically get to an excited state when hit by UV radiations and release the energy as fluorescence or heat, and, in this way, are able to dissipate a part of it and transform the rest into a non-harmful wavelength for the skin [4].

1.1.2. Inorganic Filters

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 $O_2^{-\bullet}$, $HO^{\bullet}$, and H_2O_2 [19]. There are only two mineral filters widely approved and used around the world: titanium dioxide (TiO_2) and zinc oxide (ZnO), which can be used in both micrometric (TiO_2 and ZnO) and nanometric form (n-TiO_2 and n-ZnO). In the latter, the particles can be referred to as engineered nanoparticles (NPs or ENPs) and, if they are made of TiO_2, they are often coated with inert compounds to avoid undesired chemical reactions capable of skin damage [20]. The coating often has one or two layers: the innermost, which is made of an inert material, e.g., alumina (Al_2O_3), aluminum hydroxide ($Al(OH)_3$) or silica (SiO_2) [21], and the outer, e.g., silicone, which is optional and used to give hydrophobic properties to improve the blending capacities of TiO_2 [22].

1.1.3. Other Compounds

Apart from UV filters, sunscreen lotions contain other ingredients such as preservatives, emulsifiers, colorants, foams, and perfumes [5].

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 [23–27], while sediments and SML are used because they are more suitable for the identification of lipophilic compounds released into the environment [4,5,28].

The measurement of the production of ROS species can be carried out directly or indirectly: the direct way involves spectrometry, setting the reading of the sample at a specific wavelength characteristic of each chemical species; while the indirect way predicts the determination, spectrometric [22] or chromatographic [29], of the oxidized amount of a

compound acting as a "trap" for ROS, i.e., 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-car-boxanilide (XTT) [22] and furfuryl alcohol (FFA) [29].

2.1. Mineral Filters Behavior in Water

TiO_2 and ZnO are among the most employed particles in sunscreens. These two raw materials, depending on the size used (micrometric or nanostructured), show different behaviors in water. It was evaluated that micrometric mineral filters may be released into seawater by up to 49% of the quantity used, meaning they are extremely washable [14], due to their hydrophilicity. As per the nanostructured UV filters, they can be released in the environment in variable amount from 8% up to 72%, with the cosmetic formula having a large influence on the leaching rate (mean $\pm$ SD: 45 $\pm$ 33%) [30].

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 [22]. 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 [21,31]. The presence of organic matter in water represents an important contribution for the stabilization of the particles of $nTiO_2$, which, once dispersed in water, may remain isolated or form aggregates together with macromolecules capable of forming complexes (e.g., humic acids) [32,33] 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 [21].

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 [21,34,35].

2.2. Organic UV Filters and Derivatives Behavior in Water

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 [13,36]. 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 [29,37]. 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 [29]. 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 [38–40]. 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 [40,41].

2.3. Release of Inorganic Nutrients and Metals in the Aquatic Environment

There is proof that the introduction of sunscreens into shallow-water environments lead to the release of heavy metals, purportedly present within the lotion as leftovers and production process debris, and micronutrients, such as NO_3^-, NH_4^+, and PO_4^{3-}, which are residuals derived from the degradation of some organic compounds and linked to

events of eutrophication and anomalous algal growth [4,42]. The photoprotective PCPs formulations contain not only water and sunscreens, but also a vast set of substances that are dispersed into the environment. Elements that play important biological roles, for example, Fe, Cu, N, and P, or are highly toxic to most organisms, such as Pb and Cd, can also be released [31,38]. Conservative simulations carried out for a typical Mediterranean beach showed an increase, compared to background concentrations, of close to 20% for Ti and 5% for Al. All the other elements taken into consideration also had a small increase, mostly less than 0.1% [31].

3. Biotic Compartment

The toxicity of various UV filters contained in sunscreens, both organic and inorganic, on marine organisms varies considerably depending on the UV filter and organism physiology. Many studies emphasized biological and toxicological responses, which may affect survival, behavior, growth, development, and reproduction, that were observed at various trophic levels. Coral reefs will be discussed separately in Section 4 as they are unique environments highly exposed to both climate change and human activities.

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

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

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
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	[43]
n-TiO$_2$	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)	[44]
n-TiO$_2$	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	[45]
n-TiO$_2$	Marine abalone (*Haliotis diversicolor supertexta*)	Acute toxicity stress: from 0.1 to 10 mg/L for 96 h	Oxidative stress: SOD increased (1 mg/L), GSH decreased (1 mg/L), LPO dose-dependent increase	[46]
n-TiO$_2$	Lungworm (*Arenicola marina*)	Sub-lethal OECD/ASTM 1990 acute toxicity test	Decrease in casting rate; increase in cellular damage (NRR); DNA damage in coelomocytes	[47]
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)	[48]

Table 1. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
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 0.085 mg/L; significantly lower LDH activity (p b 0.05); swimming behavior was affected by 4-MBC at low concentrations.	[49]
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	[50]
PBSA	Rainbow trout (*Oncorhynchus mykiss*)	21 and 42 days; from 1 to 1000 µg/L	Increased activity of P450 cytochromes	[51]
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 lM	[52]
BP 2-HBP BP-3 BP-4	Bioluminescent bacterium (*Vibrio fischeri*) in vitro and zebrafish (*Danio rerio*) 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. *V. fischeri* toxicity order is BP-3 > 2-HBP > BP > BP-4	[53]
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	[54]
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 µg/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	[55]

Table 1. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
BP-3	Zebrafish (*Danio rerio*)	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	[56]
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	[57]
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	[40]
BMDBM EHMC OCR	Non-biting midge (*Chironomus riparius*), oligochaete (*Lumbriculus variegatus*), and snails (*Melanoides tuberculata* and *Potamopyrgus antipodarum*).	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 (*Potamopyrgus antipodarum*) and 10 mg/kg (*Melanoides tuberculata*). BDMDM and OCR showed no effects on any of the tested organisms	[58]
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 *Daphnia*; reduction of toxic effects in the mixtures of the three UV-filters, caused by antagonistic action of the components	[59]

Table 1. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
n-TiO$_2$	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	[60]
n-TiO$_2$	Fathead minnow (*Pimephales promelas*)	Exposed to 2 ng/g and 10 mg/g body weight. Challenged with fish bacterial pathogens, *Aeromonas hydrophila* or *Edwardsiella ictaluri*	Fish mortality during bacterial challenge with *Aeromonas hydrophila* and *Edwardsiella ictalurid*; reduced neutrophil phagocytosis of *A. hydrophila*; significant histopathological alterations	[61]
n-TiO$_2$	European sea bass (*Dicentrarchus labrax*)	7 days, 1 mg/L	Chromosomal alteration	[62]
n-TiO$_2$	Marine scallop (*Chlamys farreri*)	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)	[63]
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	[64]
n-ZnO	Diatoms (*Thalassiosira pseudonana, Chaetocerus gracilis, Phaedacttylum tricornutum*)	72 h, from 10 to 80 mg/L	Growth stopped in *T. pseudonana* and *C. gracilis*; growth rate inversely proportional to NP concentration in *P. tricornutum*; Zn bioaccumulation killed *T. pseudonana*	[65]
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	[66]
n-ZnO	Green alga (*Dunaliella tertiolecta*), bioluminescent bacterium (*Vibrio fischeri*), brine shrimp (*Artemia salina*)	*V. fischeri* bioluminescence test for 5, to 30 min from 0.3 to 40 mg/L; *D. tertiolecta* algal growth test 24, 48 and 72 h from 0.1 to 10 mg/L; *A. salina* acute toxicity at 24–96 h from 10 to 100 mg/L, *A. salina* chronic exposure for 14 days from 0.03 to 0.5 mg/L	ZnO 14-day chronic exposure of *A. 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)	[67]

Table 1. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
OD-PABA OCR	Haptophyta alga (*Isochrysis galbana*), Mediterranean mussel (*Mytilus galloprovincialis*), and sea urchin (*Paracentrotus lividus*) in early stage	*I. galbana* 72 h to 2 and 90 ng/L, *M. galloprovincialis* and *P. lividus* 48 h EC_{50}	OCR was the more toxic compound for *P. lividus*; OD-PABA caused a severe negative effect on both *M. galloprovincialis* and *I. galbana*	[68]
n-TiO_2	Mediterranean mussel (*Mytilus 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	[69]
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)	[70]
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	[71]
4-MBC	Copepod (*Tigriopus japonicus*)	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 *T. japonicus*. Higher salinity levels increased the lethal, developmental, and reproductive toxicities of 4-MBC in *T. japonicus*	[72]

Table 1. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
BP-3 BEMT BMDBM MBBT OCS DHHB DBT EHT HMS OCR	Brine shrimp (*Artemia salina*) and green algae (*Tetraselmis* spp.)	*A. salina* 48 h exposure at 0, 0.02, 0.2, 2, 20, 200, and 2000 µg/L; *Tetraselmis* spp. 7-day exposure at 10, 100, and 1000 µg/L	HMS and OCR were the most toxic, followed by BMDBM, on *A. salina* 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 effects, even at high concentrations (2 mg/L).	[73]

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); diethy-laminohydroxybenzoyl hexyl benzoate (DHHB); diethylhexyl butamido triazone (DBT); ethylhexyl triazone (EHT); nanostructured titanium dioxide (n-TiO$_2$); nanostructured zinc oxide (n-ZnO).

It should be noted that most of these experiments were performed in laboratory settings and some of the UV filters were tested in isolation. Moreover, the concentrations used as stressor are usually higher than those observed in the environment.

3.1. Toxicity of Organic UV Filters

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 [74]. Studies carried out in the Hong Kong coastal area showed that the occurrence of these compounds was linked to the level of anthropogenic activities [75,76]. 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 [77] 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 [26]. 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 [23]. 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 [23].

The benthic community seems to be the most impacted by the presence of PCPs, since hydrophobic UV filters accumulate in the sediment phase [24], but the presence of UV filters may also enhance the spread of viral infection on both benthic and pelagic organisms [13]. At present, studies performed on the general formula or with a combination of UV filters are scarce both for the human body [78] and the environment [16]. Moreover, some organic UV filters seem to have estrogenic effects, but their activity and interactions in mixtures are largely unknown [55,79]. In particular, laboratory studies seemed to show that BP-3 showed anti-androgenic activities in zebrafish (*Danio rerio*) and Japanese medaka (*Oryzias latipes*) [56,57].

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, [80] with the potential to reach marine mammals [81]. 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 [82]. 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 [83]. To date, few data are available regarding the bioaccumulation and biomagnification processes, even if bioaccumulation has been detected [26,84]. This suggests that further evaluation must be undertaken to gain knowledge on the fate of these compounds along the trophic chain.

3.2. Toxicity of Inorganic UV Filters

As concerns the biotic field, particularly important is the tendency of inorganic UV filters to move vertically within the water column, starting from superficial layers, depending on surface charge, particle shape and size, and the pH and ionic strength of the water. The main problem, from a biological point of view, is that the suspended NPs can be captured by filtering organisms directly in the water column and, if not, will otherwise settle on the bottom and be taken up by detritivore organisms [85]. Studies carried out on the bivalve species *Mytilus galloprovincialis* showed the ability of the nano-TiO_2 to generate a moderate oxidative stress at concentrations of 0.2 mg/L. The stress was measured as the destabilization of the lysosomal membranes of hemocytes and digestive gland cells, and as an increase in the activity of the GST (glutathione-S-transferase) and catalase enzymes [44]. NPs, especially n-TiO_2, are strongly suspected of being bio-available and potentially gatherable by living organisms, unveiling a biomagnification phenomenon along the trophic chain [86,87].

In highly contaminated areas, their interaction with other pollutants may also be taken into consideration. A study performed in artificial seawater linked an antagonistic immune response towards 2,3,7,8-TCDD to the presence of n-TiO_2 in European sea bass (*Dicentrarchus labrax*) after 7 days in vivo exposure, suggesting that n-TiO_2 negatively influenced immune response induced by 2,3,7,8-TCDD in the spleen [88].

Zinc oxide, on the other hand, can, once released into the environment, cause very serious damage to ecosystems because it is highly toxic to bacteria and to marine invertebrates [89]. Studies on populations of the planktonic crustacean (*Daphnia magna*) fed with microalgae (*Pseudokirchneriella subcapitata*) exposed to different concentrations of ZnO showed an important reduction in the reproductive rate of the *D. magna* population [90]. These data are particularly alarming since the presence of ZnO may lead to the shrinking of planktonic organisms at the lowest levels of the trophic web, potentially causing a "cascade effect" within the whole ecosystem [64].

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 [13]. Latent infections are common in symbiotic zooxanthellans [91], 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 [13,91,92]. 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 [93]. 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 [94]. 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 [13,23,36,94,95]. 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 [96], 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 [92], 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 [97]. Moreover, the maximum photosynthetic efficiency (Fv/Fm) of symbiotic zooxanthellae in scleractinian coral (*Stylophora pistillata*) when exposed to 90 µg/L of ZnO for 35 days, was reduced by 38% as compared to the control [98]. 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 [97]. 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 [13,36].

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	[97]
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	[13]

Table 2. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
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	[96]
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	[98]
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. *caliendrum* nubbins)	No bleaching was observed in the *P. damicornis* larval tests, while bleaching was observed in the *P. 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 ≈ BP-3 > BP-4)	[92]
HMS 13% BP-3 6% OCR 5% OCS 5% BMDBM 3%	Flatworm *(Convolutriloba macropyga)*; pulse corals (*Xenia* sp.); glass anemones (*Aiptasia* spp.); Diatoms (*Nitzschia* spp.)	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 min 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	[36]

Table 2. *Cont.*

UV Filter(s)	Organism(s)	Exposure Conditions	Effects	Reference
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	[94]

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); 2-ethylhexyl 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 [72]. 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 [99] and to reduce misunderstandings on the correct use of sunscreen [100]. Furthermore, special attention needs to be given on Marine Protected Areas [77].

New conservation strategies are needed to drastically reduce the impact on ecosystems [101], 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 leg-

islation for a "coral safe" labelling might be addressed to help people make informed purchases [99]. 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.

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