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Review

# Are sunscreens a new environmental risk associated with coastal tourism?

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ABSTRACT

The world coastal-zone population and coastal tourism are expected to grow during this century. Associated with that, there will be an increase in the use of sunscreens and cosmetics with UV-filters in their formulation, which will make coastal regions worldwide susceptible to the impact of these cosmetics. Recent investigations indicate that organic and inorganic UV-filters, as well as many other components that are constituents of the sunscreens, reach the marine environment - directly as a consequence of water recreational activities and/or indirectly from wastewater treatment plants (WWTP) effluents. Toxicity of organic and inorganic UV filters has been demonstrated in aquatic organism. UV-filters inhibit growth in marine phytoplankton and tend to bioaccumulate in the food webs. These findings together with coastal tourism data records highlight the potential risk that the increasing use of these cosmetics would have in coastal marine areas. Nevertheless, future investigations into distribution, residence time, aging, partitioning and speciation of their main components and by-products in the water column, persistence, accumulation and toxicity in the trophic chain, are needed to understand the magnitude and real impact of these emerging pollutants in the marine system.



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## 1. Introduction

Throughout the history of human beings, the sun has been an object of adoration and exploration. However, it was not only a focus of admiration. Since humans lost their covering of hair and exposed their skin to sunlight they have felt the need to protect themselves, either by wearing appropriated clothes or by using paints or powders. As far as we know, the ancients Egyptians were the first to use a kind of sunscreen made of olive oil, and this was also the case in Greece and Rome. However, it was at the end of the nineteenth century when the first scientific research into sunscreen protection was reported. From

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1887 to 1934 several compounds that can be used as filters of the ultraviolet radiation (UV-filters) were discovered and in 1928 the first sunscreen was commercially available. It was during these years when international cosmetic companies were born (e.g. L'Oreal, Delial, Piz Buin, Coppertone, etc.) and when sunscreens became widely used among the general population (Rik Roelandts, 2008; Urbach, 2001). After the World War II, tanned skin became synonymous with good health and beauty in western cultures.

Nowadays, among different cosmetic products, sunscreens have been shown to give the most effective protection against ultraviolet (UV) radiation damage (Diffey, 2005). Short exposure (between 5 and 10 min) to UV radiation has therapeutic effects, i.e. it improves the production of vitamin D and this will increase calcium absorption, therefore preventing rickets in children and osteoporosis in adults. However, longer exposures can cause severe damage to skin such as skin aging, the erythema (sunburn) and/or melanoma (Holick, 2004).

Three segments compose the sun care market: sun protection, after sun, and self-tanning. This market increases every year worldwide due to the awareness of the risk associated with the sun exposure (What's Hot around the Globe: Insights on Personal Care Products. Global Service Studies Website, 2007). Cosmetic companies flood the market every year with new products, formulations and terms like "nanoparticles", "waterproof" or "broad spectrum" that generates confusion among users, who are calling for a more effective sunscreen (Kamerow, 2014).

Coastal and marine tourism is the fastest growing sector of the global tourism industry (Hall, 2001; Honey and Krantz, 2007). The number of tourists grew from 463 million in 1992 to 763 million in 2004 worldwide and it is expected that reach 1.56 billion in 2020 (Honey and Krantz, 2007). The growth of this sectordemands infrastructural development (hotels, ports, second homes, marinas, etc.), water activities and sports (i.e. recreational fishing, yachting, diving, etc.) necessary to accommodate and entertain the large number of visitors to the coastal areas. The impact caused by these activities on the coastal environment has been reported in several studies (Davenport and Davenport, 2006; Gormsen, 1997; Hall, 2001). Thus, environmental degradation and pollution (e.g. by yachts fuel, littering, seasonal increase of terrestrial runoff, etc.), destruction of habitats (e.g. destruction of coral reefs due to excessive visitations, disturbance of nearshore aquatic life, etc.), or damage to sand-dune ecosystems (e.g. lost of sandy beaches due to onshore construction), are some of the impacts of coastal tourism. Despite that coastal tourism is the fastest growing sector in the world and the sunscreen market increases every year, the implications of sunscreens as a source of new chemicals into the coastal marine system have been poorly evaluated.

### 1.1. Main components of sunscreens

Sunscreen cosmetic can be defined as: "any cosmetic product containing UV-filters in its formulation in order to protect the skin from the solar deleterious UV-light, avoiding or minimizing the damage that this radiation might cause on human health" (Salvador and Chisvert, 2005). Therefore, the most important components of the sunscreens are the UV-filters: substances with a range of light absorption in the range of UVA (400–320 nm), and/or UVB (320–280 nm), and with nearly no absorption of visible radiation (Díaz-Cruz and Barceló, 2009).

Concentration limits that can be used in sunscreen formulations depend on the different regulations worldwide (Table 1). UV-filters can be organic (classified into different families: i.e. benzophenone derivatives, salicylates, cinnamates, camphor derivatives, p-aminobenzoic acid and its derivatives, etc. (Chisvert and Salvador, 2007)), or inorganic (with only two allowed compounds: titanium dioxide ($TiO_2$) and zinc oxide (ZnO)). General usage of these inorganic components in the formulation of sunscreens is in the form of nanoparticles (nano-$TiO_2$ and nano-ZnO, with size around ≤100 nm) because they give an effective protection and they do not whiten the skin (Osterwalder et al., 2014). Because of its photocatalytic properties, $TiO_2$ nanoparticles used in sunscreens are coated with aluminum oxide or silica to prevent the formation of reactive oxygen species (ROS) (Jansen et al., 2013a). Commonly, ZnO in sunscreens are in the form of nanorods while $TiO_2$ are nanoparticles in the rutile structure (Lewicka et al., 2011). L'Oreal Group was the first company that in August 1993 patented the use of nanoparticles of metal oxides as ingredients in sunscreens (Forestier et al., 1995). The action mode of both types of UV-filters is different: while the organic absorbs a specific wavelength, the inorganic ones can give a boarder spectrum protection due to their triple action mode: reflection, scattering and absorption of the UV radiation (Manaia et al., 2013). Sunscreens are usually comprised of one or more of these UV-filters: organic, inorganic or a mixture of both. This combination increases the protection giving broad-spectrum sunscreens.

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

In sunscreen composition we can find many other ingredients such as rheology modifiers (thickeners as glycerin or fatty acids), film-forming agents as acrylates copolymer or silicones, organic UV stabilizers as benzotriazole derivatives, sensory enhancers that improve the skin feeling (i.e. silica, nylon-based compounds, etc.) and in some cases antioxidants such as vitamin C and vitamin E, which are included to reduce the oxidative stress generated by ROS formation via UV radiation. Moreover, other photoprotective agents in sunscreens provide protection from sunburn and also reduce inflammation and oxidative damage; as for example carotenoids, polyphenols, algae extracts, nicotiamide (amide form of vitamin $B_3$), vitamin A (incorporated as retinyl palmitate), selenium (in the forms of selenium sulfide or L-selenomethionine, that increase the threshold radiation dose that may produce sunburn), etc. (Chen et al., 2012; Chen and Wang, 2012; Jansen et al., 2013b; Osterwalder et al., 2014).

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

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

### 2.1. Organic UV-filters

There are 50 organic compounds allowed by different legislations to be used as UV-filters in sunscreen composition (Table 1). However, only