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Reef Safety of Zinc Oxide versus Titanium Dioxide and Organic Sunscreens

Active ingredients in sunscreens come in the following two forms: mineral and chemical filters. Each uses a different mechanism for protecting skin and maintaining stability in sunlight, but many of the common sunscreens on the market contain organic chemical filters. Common among these filters include oxybenzone, avobenzone, octisalate, octocrylene, homosalate and octinoxate. In contrast, mineral sunscreens use zinc oxide (ZnO) or titanium dioxide (TiO_2), and a handful of products combine zinc oxide with organic chemical filters. While these UV filters are excellent for protecting skin from radiation, they come with a cost. Sunscreens are washing off and contaminating coral reefs, as well as the general water supply. Organic sunscreen actives, such as oxybenzone, have been shown to have a more detrimental effect when compared to mineral sunscreens such as ZnO. Human safety is also accessed and evaluated for organic and mineral filters. Overall, ZnO is the superior choice for a reef safe sunscreen product when considering the toxicity and safety of humans and the environment.

The first issue to address involves how much sunscreen is running off beach patrons and where those sunscreen actives end up. A point of concern revolves around the statistic that 4,000 to 6,000 tons of sunscreen enters reef areas annually and about 90% of snorkeling/diving tourists are concentrated on 10% of the world's reefs [3]. Another source claims that between 6,000 and 14,000 tons of sunscreen, containing up to 10 percent oxybenzone or other actives, are estimated to be released into coral reefs each year. While much of this run-off comes from beachgoers, a large amount also comes from wastewater, which will also eventually end up in the ocean [6]. Four commonly used organic sunscreen UV filters (benzophenone-3, 4-methylbenzylidence camphor, ethylhexyl methoxycinnamate, and octocrylene) were present in a wastewater reclamation plant, indicating that UV filters are not completely removed during waste water treatment and may be carried over into the environment during the reuse applications [12]. Independent scientists have reported various concentrations of oxybenzone in waterways and fish worldwide. Oxybenzone can react with chlorine, producing hazardous reactive by-products that can concentrate in swimming pools and wastewater treatment plants [7]. Furthermore, TiO_2 and ZnO nanoparticles ($nTiO_2$/nZnO) are released from sunscreens into outdoor swimming pools and the like, which can generate reactive oxygen species (ROS); however, the negative impact of ROS in swimming pools is not significant enough to be a concern[11]. Bathing and showers also release nanoparticles, which could be seen with the detection of TiO_2 nanoparticles in a municipal sewage treatment plant [14].

As these filters enter the environment and contaminate coral reefs, organic actives are proven to be a threat to reef ecosystems. Chemical ingredients such as oxybenzone leeches coral of its nutrients and damages DNA; thus bleaching it of its fluorescent color. It has been established that only 62 parts per trillion of oxybenzone, a miniscule amount, is needed to inflict this damage [6]. Coral bleaching further exacerbates damage by promoting viral infections. It was found that organic UV filters can induce the lytic viral cycle in zooxanthellae with latent infections [8]. Zooxanthellae are single-celled dinoflagellates that live in symbiosis with marine invertebrates such as corals, jellyfish, and sea anemones [20]. In addition, oxybenzone can disrupt the development and existence of fish and other wildlife, contributing to a loss of at least 80% of the coral reefs in the Caribbean [5]. Prevention of this continuous damage would allow coral reefs to survive a long, hot summer, or allow for the recovery of a degraded area.

Mineral sunscreens may also influence coral reefs, but to a lesser known extent. Nanoparticles have a negative stigma surrounding their safety; this was demonstrated with Antaria, a popular supplier of ZnO. They were initially claiming to sell a “non-nano” form to sunscreen makers. Under pressure from Friends of the Earth Australia, they acknowledged that their ZnO would be considered a nanomaterial requiring special labeling in Europe. As for TiO_2, it must be delivered in nanoparticle form to render a sunscreen reasonably transparent on the skin [1]. Companies are choosing to avoid nanoparticles due to this stigma, all the while not acknowledging that the nano size allows for better dispersion and rubout into the skin. The safety of these particles in the environment is unclear and there hasn’t been an established study to provide substantial evidence towards either side of the debate [4]. The increased use of engineered nanoparticles in consumer products does raise the concern of environmental release and subsequent impacts. This is addressed with chemical characterization of nZnO, which forms larger aggregates in seawater than ZnO. While nZnO had a higher solubility in seawater than that of ZnO, nZnO was more toxic towards algae, but relatively less toxic towards crustaceans and fish. The toxicity of nZnO is mainly attributed to dissolved Zn^{2+} ions [2]. At high enough concentrations, ZnO encapsulated nanoparticles are shown to be toxic to mussels, but these levels are unlikely to be reached in natural marine water [10]. The effects of $nTiO_2$ on Caribbean reef-building coral have a more recognized effect. Caribbean mountainous star coral (*Montastraea faveolata*) have frequently been used as a model species to study gene expression during stress and bleaching events. Specimens of *M. faveolata* were collected in Panama and exposed for 17 days to nTiO2 suspensions. This caused significant zooxanthellae expulsion in all the colonies, but with no link to mortality in the star coral [13].

Beyond environmental toxicity, human safety must also be considered. Organic sunscreens have had a history of safety concerns among the public. Initially, these arose when a report demonstrated systemic absorption of oxybenzone in humans at a rate of 1% to 2% after topical application. The potential for biological effects was first demonstrated with a 23% increase in uterine size in immature rats after oral administration of oxybenzone [21]. This may not have an effect in humans, and penetration and retention of five commonly used sunscreen agents (avobenzone, octinoxate, octocrylene, oxybenzone and padimate O) have been tested. The concentrations of each sunscreen found in human viable epidermis after topical application was at least 5-fold lower than those appearing to cause toxicity in cultured human keratinocytes. This leads to the conclusion that the human viable epidermal levels of sunscreens are too low to cause any significant toxicity to the underlying human keratinocytes [22]. Opposingly, there is evidence that oxybenzone may remain systemically post application. The Center for Disease Control fourth national report on human exposure to environmental chemicals demonstrated that approximately 97% of the people tested have oxybenzone present in their urine [23]. This filter has also been reported to produce contact and photo contact allergy reactions, possible disruption of endocrine function, and has been linked to Hirschsprung's disease. Due to the rise in skin cancer rates and the availability of more effective sunscreen actives such as zinc oxide and titanium dioxide, doubts about the relative prevention benefit of personal care products containing oxybenzone have been raised and compared with the potential negative health and environmental effects caused by the accumulation of these chemicals in the ecosystem [7].

Another topic of human safety to consider is the effect of nanoparticles such as ZnO and TiO_2. Skin exposure to nanoparticle containing sunscreens can incorporate TiO_2 and ZnO into the stratum corneum. These particles can induce toxicity and have been sporadically observed in viable skin layers. They can be further exacerbated with long term exposure. The photocatalytic effects are especially high for TiO_2, but silica-based coatings are an effective approach to minimize these [17]. Nanoparticles have also been shown to cause lung damage when inhaled. Inhalation is more prevalent with loose powder makeup or spray sunscreens using titanium dioxide or zinc oxide of any particle size, which should be avoided. This is supported by The International Agency for Research on Carcinogens having classified titanium dioxide as a possible carcinogen when inhaled in large doses. The lungs have difficulty clearing these small particles, and they may pass from the lungs into the bloodstream. Insoluble nanoparticles can thus penetrate skin or lung tissue to cause extensive organ damage [1]. Contrastingly, there is also evidence of nanoparticles being a safe alternative to organics. One study found no evidence of significant penetration of titanium dioxide and zinc oxide nano sized particles beyond the stratum corneum, although they also stated that further studies must be done to simulate more real-world conditions such as prior UV exposure [15]. Another result showed that neither zinc or titanium ions nor microfine zinc oxide or titanium dioxide particles could penetrate porcine stratum corneum. They concluded that there was no health risk of ZnO or TiO_2 due to absence of internal exposure [16].

Both ZnO and TiO_2 seem like viable choices for a UV filter, but there are differences between these minerals. TiO_2 formulations have been shown to penetrate deeper in UVB-damaged stratum corneum. Coated and uncoated nZnO was localized to the upper one to two layers of the stratum corneum, while $nTiO_2$ reached within the epidermis and superficial dermis [18]. This indicates that ZnO may be the safer choice in terms of skin penetration. The most logical, straightforward conclusion based on data from internationally-recognized guideline studies and the current 20+ year history of human use is that nano-structured TiO2 and ZnO are safe, but there will continue to be skepticism from the public. Generally, the health benefits of sunscreens containing nano TiO2 and/or ZnO seem to outweigh human safety concerns for these UV filters [19].

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Overall, the best filter for a reef safe sunscreen is ZnO. Sunscreens made with zinc oxide and titanium dioxide have many distinguishing features. They provide strong sun protection with fewer health concerns and have greater photostability. Zinc oxide can provide greater protection from UVA rays than titanium oxide or any other sunscreen chemical approved in the U.S. to date. Sunscreen makers use zinc oxide nanoparticles to formulate lotions with less of a white tint and a better dispersion [1]. These nanoparticles have an inconclusive but seemingly harmless effect on ocean and human life if made and used properly. On the other hand, organic sunscreens such as oxybenzone can cause coral bleaching, with expulsion of zooxanthellae. There is also possible allergenic potential or disruption of endocrine function with absorption and skin penetration of organics. There is good evidence that little, if any, zinc or titanium nanoparticles penetrate the skin to reach living tissues. Mineral sunscreens are thus the more prominent choice for a manufacturer, but it is important to use forms of minerals that are coated with inert chemicals to reduce photoactivity and avoid skin damage. To date, no such problems have been reported [9]. Reef safe sunscreen products should use ZnO as the best and most reef friendly choice of filter.

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