

# Dermatological and environmental toxicological impact of the sunscreen ingredient oxybenzone/benzophenone-3

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## Summary

Oxybenzone (Benzophenone-3) is an emerging human and environmental contaminant used in sunscreens and personal care products to help minimize the damaging effects of ultraviolet radiation. 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, and independent scientists have reported various concentrations in waterways and fish worldwide. Oxybenzone can also react with chlorine, producing hazardous by-products that can concentrate in swimming pools and wastewater treatment plants. Moreover, adverse reactions could very well be increased by the closed loop of ingesting fish contaminated with oxybenzone and/or washing the ingredient off our bodies and having it return in drinking water as treatment plants do not effectively remove the chemical as part of their processing protocols. In humans, oxybenzone has been reported to produce contact and photocontact allergy reactions, implemented as a possible endocrine disruptor and has been linked to Hirschsprung's disease. Environmentally, oxybenzone has been shown to produce a variety of toxic reactions in coral and fish ranging from reef bleaching to mortality. Lastly, with the rise in skin cancer rates and the availability of more effective sunscreen actives such as micronized zinc oxide and titanium dioxide, serious doubts about the relative prevention benefit of personal care products containing oxybenzone must be raised and compared with the potential negative health and environmental effects caused by the accumulation of this and other chemicals in the ecosystem.

## KEYWORDS

contact dermatitis, environmental contaminant, toxicity

## 1 | INTRODUCTION

Consumer awareness about human health and environmental concerns associated with various ingredients used in personal care products is increasing markedly. Several state and Federal laws banning the use of polyethylene microbeads in cleansing scrubs, tooth pastes, and other consumer products were instituted in 2016 as a result of their presence in numerous fish species found in the food supply and the associated potential adverse health effects to humans.<sup>1</sup> In 2017, several bills have been introduced in the Hawaiian legislature

that are designed to ban the use of oxybenzone in any consumer product—particularly if the intended use is near beaches—or, at a minimum, requiring a warning label stating that the chemical is harmful to coral and the aquatic environment. Oxybenzone is an aromatic hydrocarbon that acts as an ultraviolet (UV) light filter in sunscreen formulations. As would be expected, there has been significant debate regarding these proposed actions, with environmentalist calling for a ban on the chemical, industry voices questioning the scientific validity of the negative human/environmental toxicity data based on limited safety data conducted 20 to 40 years ago, and the

medical profession expressing concerns related to increasing the rate of skin cancer should UV blockers, like oxybenzone, be removed from sunscreen formulations. The present review examines the scientific evidence related to oxybenzone and posits that alternative formulation strategies using micronized zinc oxide and/or titanium dioxide are available which avoid the toxic effects. It is hoped that this examination will be useful to the dermatology community as it considers how to best respond to patient questions related to human health and environmental concerns associated with the use of oxybenzone.

## 2 | GENERAL INFORMATION

Common Name used on Drug Labels (Active Ingredient): Oxybenzone.

Common Name used on Non-Drug Labels (INCI Name): Benzophenone-3.

Common Technical/Chemical Name: 2-Hydroxy-4-Methoxyphenyl Phenylmethanone.

Common Trade Names: Eusolex 4360 and Escalol 567.

Chemical Abstract Service (CAS) Number: 131-57-7.

Molecular Weight (MW): 228.26 Daltons (g/mol).

## 3 | USES

Oxybenzone is commonly used as a short-wave (290 to 320 nm) ultraviolet light (UVB) and mainly short-wave UVA light (320 to 340 nm) absorber at concentrations up to 6% in sunscreen preparations and up to 0.5% in personal care products as a photo-stabilizer minimizing color and odor changes. It has been reported to be used in over 2000 personal care formulations spanning numerous product categories from skin and hair care to color cosmetics and fragrances. Additionally, it is used in plastics as an ultraviolet light absorber and stabilizer. In 1990, oxybenzone was added to the Environmental Protection Agency High Production Volume Challenge Program which identifies ingredients manufactured or imported into the United States in amounts equal to greater than one million pounds per year.

## 4 | UV ABSORPTION SPECTRUM, SUNSCREEN EFFICACY TESTING, AND SKIN CANCER RATES

With the recent attempts in Hawaii to ban the use of oxybenzone in sun protection factor (SPF) products, some have expressed concern over losing an effective UV absorber and possibly causing an increase in the number of skin cancers observed annually. The ability of a sunscreen product to protect against UV rays is not based on an individual ingredient contained in a formula, however, but rather how the formula performs, as a whole, when tested according to the Food & Drug Administration (FDA) guidelines for labeling and

effectiveness testing; sunscreen drug products for over-the-counter human use.<sup>2</sup> For example, a product could contain the most effective UV-absorbing ingredients allowed (avobenzene, titanium dioxide, or zinc oxide), but if it is formulated in an inappropriate way that product would deliver little to no protection from the damaging effects of UV rays. This reality underlies why FDA has established these guidelines and requires as a matter of law that all formulas be tested for efficacy and stability prior to being sold in the marketplace. Therefore, any product sold in the United States that claims a SPF and, further, makes a broad spectrum claim—regardless of the ingredient(s) used in the product—can be trusted to perform according to the package labeling and protect against the carcinogenic effects of the sun.

It is important to note that SPF testing (UVB) is conducted in 10 human subjects, as outlined in the FDA testing guidelines. However, broad spectrum (UVA) testing is an analytical method (in vitro) that measures if a product has a critical wavelength of at least 370 nm, which represents 90 percent of the total area under the curve in the UV region. Based on the FDA definition, only zinc oxide, titanium dioxide, avobenzene, menthyl anthranilate, oxybenzone, and octocrylene would qualify out of all the approved actives noted in the sunscreen monograph (Table 1). It is important to note that based on these classification criteria, oxybenzone just makes the critical wavelength cutoff of at least 370 nm for UVA claims and would be tied for last place with octocrylene in terms of broad spectrum performance.

The average annual number of adults treated for skin cancer in the United States increased from 3.4 million in the 2002-2006 time period to 4.9 million annually between 2007 and 2011.<sup>4</sup> Correspondingly, the average annual total cost for managing skin cancer increased 126.2% from \$3.6 billion to \$8.1 billion. Importantly, the National Cancer Institute<sup>5</sup> consumer use data for adults aged 18 years or older between the years 2005 and 2015 report that 70.8% of all adults practice one of the three sun protective behaviors identified: (i) seeking shade and avoiding sun during peak hours (ii) wearing protective clothing; and (iii) using sunscreen. Of the three methods, only 33.7% reported applying sunscreens, while 38.4% relied on clothing and 39.1% usually sought shade.

Taking into account how products are tested for UV efficacy, the absorption spectrum of the currently approved FDA actives, and how

**TABLE 1** Critical wavelength for commonly used UV filters with an attenuation of 370 nm and above<sup>3</sup>

FDA monograph sunscreen ingredients drug label name (INCI/Common Name)	Attenuation in NM	Peak absorption
Octocrylene	290-370	305-325
Oxybenzone (Benzophenone-3)	290-370	290-300 & 325-340
Menthyl anthranilate	290-380	340-350
Avobenzene (Butyl Methoxydibenzoylmethane)	290-390	355-370
Titanium dioxide	290-400	290-320
Zinc oxide	290-400	290-385

consumers actually deal with protecting against sun exposure, it is unclear that products containing oxybenzone offer any distinct benefits over other available options when it comes to reducing elevated epidemiological trends in skin cancer. Indeed, for those sunscreen users who have concerns and want the strongest UV protective against the sun, zinc oxide has the best UV attenuation (290–400 nm) and peak absorption (290–385 nm) of all actives, covering 100% of the UVB and 95% of the UVA spectrum. Zinc oxide can be used individually or with other actives, if UV protection above an SPF 30 is required for very sun sensitive individuals, and with the advent of micronized particles (100 nm or larger) product, esthetics are excellent and promote patient compliance. Lastly, it is more likely that patients would receive better protection from frequent application of sunscreens rather than solely relying upon higher SPF factors. For example, a product with a SPF 30 protects against 97% of UVB whereas a product with a SPF 50 protects against 98%; however, to gain that additional 1%, a SPF 50 product may contain almost twice the concentration of sunscreen actives, potentially increasing the chance of adverse reactions, particularly in patients with sensitive skin.

## 5 | SKIN REACTIVITY

In a study designed to describe allergens associated with a sunscreen source, the North American Contact Dermatitis Group evaluated both active and inactive ingredients in sunscreen products that may cause contact dermatitis. Standard patch testing in 23 908 patients was conducted between 2001 and 2010 and identified 219 (0.9%) positive reactions. The top three most frequent allergens in sunscreens were as follows: oxybenzone (70.2% for 10% concentration, 64.4% for 3% concentration), DL-alpha-tocopherol (4.8%), and fragrance mix I (4.0%).<sup>6</sup>

Similarly, the European Scientific Committee on Consumer Safety (SCCP) published an opinion paper<sup>7</sup> based on a review of 20 publications involving 6378 patients that were photo-patch tested for oxybenzone and other sunscreen actives between the 1981 and 2003. A total of 159 positive reactions were noted, leading to the conclusion that oxybenzone is a photoallergen. By way of comparison, only 19 photoallergic reactions were noted in these studies to p-aminobenzoic acid (PABA) and 34 photoallergic reactions to the various PABA esters.

Verhulst and Goossens<sup>8</sup> recently published a review and update of cosmetic products that have been reported to produce contact urticaria. Causative agents cited included phenoxyethanol, polyaminopropyl biguanide, oxybenzone, menthol, and a number of plant-derived ingredients including wheat and wheat protein hydrolyzates. Evidence of contact urticaria and, to a lesser degree, contact-mediated anaphylaxis was reported to be caused by oxybenzone.

The American Contact Dermatitis Society listed benzophenones as the 2014 Allergen of the Year, covering both allergy and photoallergy reactivity based on research reported by Heurung et al<sup>9</sup> They sighted oxybenzone (benzophenone-3) as the most frequent reactor in the class as well as the most prominent agent found in 68% of the 201 sunscreen products assessed. The authors also noted that oxybenzone showed high rates of cross-reactivity with the sunscreen

active octocrylene, as well as ketoprofen, a topical nonsteroidal anti-inflammatory.

Additionally, oxybenzone has a molecular weight (MW) of 228.26 daltons, which raises concerns historically as a MW below 500 daltons has been associated with most of the common contact allergens.<sup>10</sup>

Cumulatively, there appears to be sufficient research demonstrating that oxybenzone possesses the potential to induce/elicite contact allergy, photocontact allergy, and contact urticaria reactions in humans. To put this into perspective, the sunscreen active p-aminobenzoic acid (PABA) and its esters have also been reported to produce allergic contact and photocontact dermatitis reactions<sup>7,11</sup> at somewhat lower reactivity rates than oxybenzone; however, PABA was forced into obscurity in the United States as a result of concerns from the medical community about sensitivity and subsequent competitive pressures on industry.

## 6 | ENVIRONMENTAL CONCERNS

In order to be effective, SPF products must be formulated to stay on the surface of the skin where they can reduce the penetration of UV energy to the underlying tissue. Therefore, when formulated in an effective SPF vehicle, oxybenzone demonstrates little absorption through the skin despite having a low MW. Gonzalez et al<sup>12</sup> observed an average excretion rate of 3.7% of the dose of a commercial sunscreen containing 4% oxybenzone when applied morning and night for 5 days. Accordingly, it is possible to estimate that if approximately 4% of oxybenzone in a sunscreen formulation is absorbed into the skin, 96% of the remaining dose is available to be washed off and enter various waterways. Corroborating this point, a 2008 study estimated that 4000 to 6000 tons of sunscreens were washed off in tourist reef areas annually<sup>13</sup>; as of 2017, scientists are currently estimating that 8000 to 16000 tons of sunscreen enter coral reefs each year.<sup>14</sup> The increase is the result of the continued growth of the global sunscreen market, which is projecting to reach sales of \$11 billion by the year 2020. To better understand the implications of these figures, Tsui et al<sup>15</sup> sampled the waters of eight cities across four countries (China, United States, Japan, and Thailand) and the North American Arctic identifying twelve widely used aromatic hydrocarbon UV chemical filters. In general, concentrations of the chemicals increased with population density. Oxybenzone concentrations ranging from as high as 33 parts per trillion (ppt) in the Arctic to 5 parts per billion (ppb) in Hong Kong were identified. It should be noted that the surface waters sampled came largely from metropolitan areas featuring both commercial and industrial development, as opposed to beach or resort communities that see high levels of recreational water use by humans. Moreover, the concentrations in the Arctic waters suggest significant migration of toxic chemicals is occurring as current and tidal forces lead to water migration. The authors concluded that the findings represent various ecological risks to marine ecosystems, including promoting coral bleaching and adversely affecting reproduction in fish.

In 2008, Danovaro et al<sup>13</sup> were one of the first to report that oxybenzone had a negative impact on coral causing bleaching and death at concentrations of 33 and 50 parts per million (ppm). Additional research published in 2015 by Downs et al<sup>16</sup> identified oxybenzone as a phototoxicant, genotoxicant, and a skeletal endocrine disruptor in coral. They determined a lethal concentration 50 (LC50) for coral larvae that ranged from 139 to 3100 ppb depending on the specific test conditions. Coral cell LC50s for seven different coral species ranged from 8 to 340 ppb. The authors went on to measure the amount of oxybenzone at various locations (bays and open waters) at two different locations: Concentrations in the sampled waters from the U.S. Virgin Islands ranged from 75 to 1400 ppb and the Hawaiian Islands 0.8 to 19.2 ppb. Based on these findings, the water concentration of oxybenzone currently in the Virgin Islands overlaps the LC50 calculated for coral larvae and coral cells, while the waters in Hawaii are starting to reach levels that are within the range of the LC50 for coral.

The identification and accumulation of oxybenzone in waters cause concerns not just to coral, but to many other aquatic species as well. Braush and Rand<sup>17</sup> reviewed oxybenzone toxicity in *Daphnia magna* (invertebrate) and *Oncorhynchus mykiss* and *Oryzias latipes* (fish) and found LC50s of 1.9 ppm, 749 ppb, and 620 ppb, respectively. The authors further identified that UV filters have been shown to have bioaccumulation factors greater in fish than in water. For example, Gago-Ferrero et al<sup>18</sup> evaluated the accumulation of UV absorbers in a variety of fish in Spain and were able to extract oxybenzone from the tissue of white fish, rainbow trout, barb, chub, perch, and mussels. Taken together, these studies suggest the potential for increasing concentrations in species higher up in the trophic level, with humans poised to ingest the highest concentrations from the larger species that are regularly fished for human consumption.

UV filters enter the environment in two primary ways, directly from sloughing off while swimming around reefs or other waterways and indirectly via wastewater treatment plant (WWTP) effluent. In fact, even swimming in chlorinated pools and people washing sunscreens off their bodies while bathing raises several concerns. Researchers have observed that chlorine can react with oxybenzone producing chlorinated oxybenzone, which results in significantly more cell death than unchlorinated controls.<sup>19</sup> Another study evaluated oxybenzone transformation and kinetics after chlorination.<sup>20</sup> These results indicated that more genotoxic transformation products were produced in spite of the elimination of oxybenzone, posing potential threats to drinking water safety. Similarly, six water treatment plants in southeast Brazil evaluated WWTP levels of oxybenzone and observed (0.18 to 1.15 ppb) in both raw treated and chlorinated water, indicating that the compound was not removed by the water treatment process.<sup>21</sup> Additionally, Braush and Rand<sup>17</sup> reported that Switzerland estimated the input of 69 g of oxybenzone per 10,000 people per day into their WWTP.

The Centers for Disease Control and Prevention evaluated urinary samples obtained from 2517 participants aged 6 years and

older between 2003 and 2010 and identified oxybenzone levels ranging from 15 ppb up to 3 ppm.<sup>22</sup> Meeker et al<sup>23</sup> recruited 105 pregnant women in northern Puerto Rico to provide urine samples and complete questionnaire data at three times during gestation. Urinary concentrations of oxybenzone ranged from 41.0 to 66.4 ppb and a positive association between biomarker concentrations, and self-reported use of personal care products was reported. An intraclass correlation coefficient (ICC) of 0.62 was determined for oxybenzone which was the highest among all the chemicals identified in the study. In contrast, urine samples were collected from 33 young Danish men over a 3-month period<sup>24</sup> with ICCs ranging from 0.69 to 0.80 and with more than 70% of the urine samples having detectable levels of oxybenzone. These data suggest that while most oxybenzone in personal care products is not significantly absorbed, sufficient quantities do enter the body such that meaningful levels can be measured in urine that finds its way to WWTP. Oxybenzone and/or its metabolite 4-methylbenzophenone may be more ubiquitous than generally thought (e.g., not just in sunscreens, cosmetics, and fragrances). The International Agency for Research on Cancer<sup>27</sup> has identified several sources of dietary exposure to these molecules in food or addition to food as a flavoring agent, its presence in drinking water as a contaminant, and through its migration from food packaging, printing inks, or recycled paperboard.

Kim and Choi<sup>25</sup> observed that oxybenzone has been detected in water, soil, sediments, sludge, and biota. Based on their review, the maximum detected level in ambient freshwater and seawater was 0.13 ppb and 0.58 ppb, respectively, and in wastewater, influent was 10.4 ppb. They also noted that in humans, oxybenzone has been detected in urine, serum, and breast milk samples worldwide with receptor binding assays showing strong adverse endocrine effects, including anti-androgenic and anti-estrogenic activity. Predicted no-effect concentration (PNEC) for oxybenzone was derived at 1.32 ppb; the levels observed in ambient water are generally an order of magnitude lower than the PNEC, but in wastewater influents, hazard quotients greater than 1 were noted. Lastly, Huo et al<sup>26</sup> looked at the relationship between maternal oxybenzone exposure and Hirschsprung's disease (HSCR) as well as its potential mechanism. HSCR is a neonatal intestinal abnormality that is derived from the failure of enteric neural crest cells migration to hindgut during embryogenesis from 5 to 12 weeks. The results showed that maternal oxybenzone exposure was associated with offspring developing HSCR, likely due to the chemical's inhibiting migration of highly specific cells.

## 7 | CONCLUSION

Based on the data reviewed, oxybenzone can be found globally in water, soil, sediments, sludge, and biota as well as in human urine, serum, and breast milk. As a sunscreen active, it is not as effective at protecting against UVA exposure as avobenzone, titanium dioxide, and/or zinc oxide. In humans, the chemical has been linked to Hirschsprung's disease is a confirmed contact allergen and photocontact allergen with some potential to induce contact urticaria and, to

a lesser degree, contact-mediated anaphylaxis. Environmentally, oxybenzone inhibits reproduction of coral and fish via embryo toxicity and/or causing male fish to be feminized, coral bleaching, and/or death. In summary, the potential negative health and environmental effects caused by the accumulation of this and other chemicals in the ecosystem needs to be taken into consideration by industry and regulatory agencies prior to the development and release of new and effective personal care products.

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