Oxybenzone contamination from sunscreen pollution and its ecological threat to Hanauma Bay, Oahu, Hawaii, U.S.A.

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Abstract

Hanauma Bay is a 101-acre bay created by the partial collapse of a volcanic cone and once supported a vibrant coral reef system. Hanauma Bay is the most popular swimming area in the Hawaiian Islands and has been reported to have averaged between 2.8-3.5 million visitors a year in the late 1980s and 1990s. In the 2010s, visitors averaged between 3,000-4,000 a day and peaked around 10,000-13,000 per day. Concentrations of oxybenzone and other common UV filters were measured in subsurface water samples and in sands from the beach-shower areas in Hanauma Bay. Results demonstrate that beach showers also can be a source of sunscreen environmental contamination. Hydrodynamic modeling indicates that oxybenzone contamination within Hanauma Bay's waters could be retained between 14 and 50 hours from a single release event period. Focusing on only oxybenzone, two different Hazard and Risk Assessment analyses were conducted to determine the danger of oxybenzone to Hanauma Bay's coral reef system. Results indicate that oxybenzone contamination poses a significant threat to the wildlife of Hanauma Bay. To recover Hanauma Bay's natural resources to a healthy condition and to satisfactorily conserve its coral reef and sea grass habitats, effective tourism management policies need to be implemented that mitigate the threat of sunscreen pollution.

Key Words: Hanauma Bay, coral, sunscreen, oxybenzone, risk assessment, hydrodynamic modelling

Introduction

Hanauma Bay is a 101-acre bay created by the partial collapse of a volcanic cone and once supported a vibrant coral reef system. In 1967, it was designated as Hawaii's first Marine Life Conservation District and is located within the U.S. Hawaiian Islands Humpback Whale National Marine Sanctuary. It is critical coral reef habitat, as well as habitat for Hawaiian Monk Seals and Green Sea Turtles. Hawaii's Clean Water Act (Chapter 11-54-3(c)(1) Hawaii Administrative Rules) classifies Hanauma Bay's water as Class AA waters, which needs to "…remain in their natural pristine state as nearly as possible with an absolute minimum of pollution or alteration of water quality from any human-caused source or actions."

Hanauma Bay is the most popular swimming area in the Hawaiian Islands and was reported to have averaged between 2.8-3.5 million visitors a year in the late 1980s and 1990s (Mak & Moncur, 1995). In the era of the late 2010s, accurate visitor statistics are difficult to access, but most sources report at least an average of between 3,000 to 4,000 visitors a day and peaking around 10,000-13,000 per day. In the era of COVID-19, the bay had been closed to all visitors from March, 2020 to December, 2020. Most of these visitors use over-the-counter sunscreen products for ultraviolet light (UV) sun-protection. As recommend by the U.S. Food & Drug Administration, these products should be applied to an average sized, relatively bare-torso swimmer in amounts of about 36 grams every 90 minutes (U.S. FDA 2019). This is predominantly because swimming and sweat-inducing activities causes the discharge of the sunscreen product from the skin into the environment, reducing the Sun-Protection Factor efficacy of the product (U.S. FDA 1978).

Sunscreen products predominantly use UV-filter drugs such as oxybenzone, avobenzone, octocrylene, octinoxate, octisalate and homosalate. The increasing use of sunscreen UV-filter drugs has triggered concern about their emissions into the environment (Molins-Delgado et al.,

2016). As a consequence of their constant use and uninterrupted release, these chemicals are classified as pseudo-persistent environmental pollutants, and nowadays constitute one of the most important chemical families designated as contaminants of emerging concern by the U.S. EPA (Blitz and Norton, 2008; Diaz-Cruz and Barceló, 2015).

Before 2019, oxybenzone (benzophenone-3; 2-hydroxy-4-methoxphenyl phenylmethanone; CAS No. 131-57-7) was one of the dominant UV-filters used in sunscreen products. In the U.S. and E.U., oxybenzone concentrations are regulated at 6% in sunscreen and cosmetic products (European Union, 2019). In Australia, oxybenzone concentrations have a maximum concentration of 10%, while Japan allows for no more than 5% (Australian Government, 2013; Japan, 2000). A 2016 investigation into the contamination of Hanauma Bay saw water-column oxybenzone concentrations of more than 1,600 ng/L, and avobenzone concentrations were above 1,500 ng/L (Booth & Manning, 2017). The amount of daily-swimming activity, estimated swimmer discharge rates, and the preliminary UV-filter survey makes pertinent the dilemma of whether swimmer and beach activity pose a potential threat to the sustainability of Hanauma Bay's coral reef ecosystem and marine mammal and sea turtle habitats.

The danger of UV-filters to wildlife receptors has been known for at least the past 20 years, starting with the works of Schlumpf, Fent, and others, which demonstrated that UV-filters such as oxybenzone can cause endocrine disruption in vertebrate systems and developmental toxicity in fish (Schlumpf et al., 2001; Schreurs et al., 2002; Ma et al., 2003, Schlumpf et al., 2004; Kunz et al., 2006; Kunz & Fent, 2006). A number of studies show that oxybenzone poses a realistic hazard by either inducing acute toxicity or acting as an endocrine/developmental disruptor to aquatic and marine invertebrates, including sea urchins, bivalves, and arthropods (Li, 2012; Bošnjak et al., 2013; Ozáez et al., 2014; Paredes et al., 2014; Lopes et al., 2020;

O'Donovan et al., 2020; Thorel et al., 2020). Oxybenzone is also toxic to a wide number of algae and plants, including marine phytoplankton and macroalgae (Mao et al., 2017; Zhong et al., 2019a; Zhong et al., 2019b; Zhong et al., 2020; Teoh et al., 2020). Oxybenzone can be detrimental to corals, ranging from mortality, bleaching, and gross planula deformations to genotoxicity, endocrine disruption and significant shifts in its metabolome (Donavaro et al., 2008; Downs et al., 2016; He et al., 2019a; He et al., 2019b; Stien et al., 2020; Wijgerde et al., 2020). Sunscreen pollution can also impact endangered species, such as sea turtles and marine mammals (Alonso et al., 2015; Cocci et al., 2020). Finally, emerging science has demonstrated a detrimental interaction between oxybenzone toxicity and climate change factors, such as elevated temperatures and ocean acidification (Chaves Lopes et al., 2020; Wijgerde et al., 2020).

The Hazard Identification is a critical element of the investigative and management process in addressing the issue of environmental contamination by sunscreen products. The goal of a Hazard Identification is to allow for the construction of a scientifically defensible argument regarding exposure of specific wildlife receptors to a discrete contaminant which can cause a toxicological/pathological response ((NRC, 1983; U.S. EPA, 1992, 1998, 2004; NRC, 2009; European Commission, 2019). Hazard Identification analysis also helps to recognize the specific pathologies a chemical contaminant may cause to relevant ecological receptors during a field investigation. For example, are the levels of a sunscreen contaminant (e.g., oxybenzone) in an area high enough to induce mortality, genotoxicity, coral bleaching, decreases in photosynthetic conditions, or developmental deformities? One of the applications of the results of a Hazard Assessment is for Hanauma Bay resource managers to identify and implement effective mitigation measures to reduce contamination levels to ensure some level of safety for Hanauma's ecological integrity.

In this study, we measured concentrations of oxybenzone, other benzophenone chemical species, and a group of benzotriazoles in subsurface water samples that were collected in the back reef zone most utilized by swimmers in Hanauma Bay. We measured the levels of oxybenzone and other common UV filters in sand samples in the beach-shower area in Hanauma Bay, to determine if this could be a second source of sunscreen contamination. We also conducted a preliminary examination of the retention time of oxybenzone (and other sunscreen compounds) within Hanauma Bay. Focusing only on oxybenzone, environmental contamination data were combined with the ecotoxicological data from the published literature, and then applied to a Hazard and a Risk Assessment to determine the danger of oxybenzone to Hanauma Bay's coral reef system.

Materials and Methods

Sample Collection

Seawater samples from Hawaii were collected using precleaned one-liter amber glass bottles with Teflon lined lids (I-Chem, 300 series, VWR). Sample locations are indicated in **Figure 1A**. Samples were collected approximately 30 cm below the surface of the water on November 17, 2017, between 16:00 and 17:30 Pacific Standard Time.

Wate sample extraction

Sample volumes of 100-200 mL were loaded onto Strata™-X 33 µm polymeric reversed phase C18 cartridges (500 mg/12 mL;Phenomenex) to extract, purify and concentrate the target analytes by solid phase extraction (SPE). After loading, the cartridges were washed with 3 mL of HPLC-grade water and dried under a gentle current of nitrogen. Then, the analytes were eluted with (a) 7.5 ml of a solution of ethyl acetate and dichloromethane 1:1 v/v (EtAc:DCM (1:1)) and (b) 2 ml of DCM. The extracts were joined and evaporated with nitrogen until near dryness and then transferred into a LC-vial prior to full evaporation. Reconstitution was performed with 0.5 ml of HPLC-grade water containing the isotopically labelled internal standards. Finally, 20 µl of the extracts were analyzed by HPLC-MS/MS.

Water sample extract analysis by HPLC-MS/MS

The determination of the target compounds was accomplished by high performance liquid chromatography-tandem mass spectrometry in a Symbiosis Pico chromatograph from Spark Holland (Emmen, The Netherlands) operated in off-line mode, and coupled to a 4000 Q TRAP™ mass spectrometer from Applied Biosystems-Sciex (Foster City, CA, USA). The chromatographic separation was achieved on a LiChorCART ® Purospher® STAR® RP-18 EC

(125 mm x 2.0 mm, 5 µm) from Merck (Darmstadt, Germany), preceded by a guard column LiChorCART® 4-4 Purospher® STAR® RP-18 ec (5 µm). The mobile phase consisted of water and acetonitrile (ACN) both HPLC grade with a 0.1% formic acid. The chromatographic gradient was as follows: the initial conditions of 5% ACN, increasing to 75% in 7 minutes, and to 100% in the next 3 minutes. Pure organic conditions were kept constant for five minutes and in the next two minutes until initial conditions were reached. The analytes were determined using electrospray ionization (ESI+) under positive mode and selected reaction monitoring (SRM) mode for improved sensitivity and selectivity. Two transitions per compound were registered, the more intense for quantification and the second one for confirmation.

Quality control/quality assurance for LC-MS analysis of water samples

Quantification was conducted through internal-standard calibration using isotopically labelled standards (**Supplemental Table 1**). The total run time for each sample was 23 minutes. The method performance is shown in (**Supplemental Table 2**).

Sand sample extraction analysis by HPLC-MS/MS

Benzophenone (BP, CAS# 119-61-9), Tinosorb M (methylene bis-benzotriazolyl tetramethylbutylphenol; CAS# 103597-45-1), and oxybenzone (CAS# 131-57-7) were purchased from Sigma-Aldrich (Lyon, France), while Tinosorb S (bis-ethylhexyloxyphenol methoxyphenyl triazine; CAS# 187393-00-6), avobenzone (butyl methoxydibenzoylmethane; CAS# 70356-09-1), homosalate (CAS# 118-56-9), octisalate (ethylhexyl salicylate; CAS# 118-60-5) and octocrylene (CAS# 6197-30-4) were kindly provided by Pierre Fabre Laboratories. Butyloctyl

147 salicylate (CAS# 190085-41-7)) was obtained from Innospec Active Chemicals. Octinoxate
148 (ethylhexyl methoxycinnamate; CAS# 5466-77-3) was obtained from Accustandard (Cat#
149 ALR144N).

150 Initial analysis of samples from beach sites 1, 2, and 3 exhibited extremely high
151 concentrations of several of the UV filter analytes that were above the highest concentration
152 calibrant (**Figure 1B**). For beach samples sites #1, #2, and #3, 0.2 grams of sand were used for
153 extraction. For beach sand sample #4, two grams of sand was used. For each sand sample, 7
154 replicates were extracted and analyzed. In all cases, sands were not dried before being added into
155 the extraction tubes. If need be, excess water was removed by spreading the sand on a filter
156 paper. Sands were extracted with MeOH (2 mL) and the concentration of UV filters in the
157 supernatant was measured by direct injection in UHPLC-HRMS following the protocol
158 previously described (Rodrigues et al., 2021). The concentration in the supernatant was
159 calculated by comparison of peak areas with those from an external calibration curve. After
160 analysis, the solvent and the sand water were removed by evaporation with a GeneVac HT-4X.
161 The exact mass of dry sand gave the initial mass of water in the sand and the total volume of
162 supernatant (2-mL MeOH + sand water), allowing for correction of the concentrations in
163 supernatant and in sand.

164

165 **Quality Control/Quality Assurance for LC-MS analysis of water samples**

166 The limits of detection (LOD) and quantitation (LOQ) are provided in **Supplemental**
167 **Table 3**. The recovery rates were calculated from spiked sand samples, which were extracted
168 with MeOH using the same protocol as for extraction of natural sand samples (Rodrigues et al.,
169 2021). The recovery rates were 85 % for homosalate, 88 % for benzophenone and 100 % for

Tinosorb M, avobenzone, oxybenzone, butyloctyl salicylate, octinoxate, octisalate, Tinosorb S, and octocrylene (**Supplemental Table 3**).

Pollution retention modeling

Both the particle pathway and retention will affect how released pollutants influence local water quality and ecosystem health (Du et al., 2019). A 2DH hydrodynamic and particle tracking model was implemented to estimate the mixing and dispersion of sunscreen in the water of Hanauma Bay (Tsanis et al., 2007; Jiang et al., 2017). The model developed for this study solves the Navier-Stokes equations for shallow water with the hydrostatic pressure assumption. The computational grid is shown in **Supplemental Figure 1**. An ocean model should provide a realistic large-scale circulation while also resolving small-scale flow features down to the scale of individual reefs. Unstructured-mesh ocean-models offer a potential solution to this resolution issue by locally increasing the model resolution close to reefs and islands (Lambrechts et al., 2008; Thomas et al., 2014, 2015). Bathymetry data were acquired from U.S. NOAA's National Centers for Environmental Information (NCEI, https://www.ncei.noaa.gov/). For deeper areas, we used the General Bathymetric Chart of the Oceans database (https://www.gebco.net/). The sunscreen contaminant release data used in the model were from water sample sites #1, #4, #6, #8, and #10 (**Figure 1A**).

The dispersion model was run for an arbitrary one-month period in 2018, including periods of tide-dominant and oceanic-current-dominant conditions. During periods of oceanic-current domination, a strong shoreward tendency can be observed in current behavior for this area. To illustrate this, three hydrodynamic models were run to determine oxybenzone retention within Hanauma Bay to tidal forcing (Model scenario #1), a combination of tidal and (southward) oceanic current forcing (adopted from global HYCOM data) (Model scenario #2),

193 and a combination of tidal and (southward) oceanic current forcing (adopted from global
194 HYCOM data), but during periods of relatively strong shoreward (northward) current presence
195 (Model scenario #3).

196

197 **Hazard and Risk Methods**

198 For a hazard assessment, there are a number of diverse approaches in calculating a hazard (or
199 risk) quotient (Environment Canada 2013; European Commission 2003; European Medicines
200 Agency 2006; Dussault et al. 2008; Hernando et al. 2006; USEPA 2004, 2020). In this paper, we
201 compare two different hazard/risk-quotient assessment methods to determine the threat to
202 wildlife integrity for Hanauma Bay.

203 The definition of a hazard or risk quotient is "the ratio of the potential exposure to a
204 substance and the level at which no adverse effects are expected" (U.S. EPA, 2018). Hazard
205 quotient equations require at least two parameters: (a) measured environmental concentration
206 (MEC) and (b) a toxicity endpoint (e.g., No observed effect concentration, lethal concentration
207 for 50% of the population (LC_{50})). Measured environmental concentrations used for these
208 calculations are found in **Figure 1A**.

209 The first method employed a Hazard Quotient (HQ) calculation following a protocol
210 specified by the U.S. Environmental Protection Agency (U.S. EPA) guidance for pesticides and
211 other chemicals (U.S. EPA, 2004). This guidance also makes provisions for determination of
212 effects for Endangered and Threatened species (U.S. EPA, 2004). This method compares the
213 MEC to an acute toxicity endpoint (e.g., LC_{50} is the concentration of a chemical where 50% of
214 the organisms die) or EC_{50} concentration of a chemical (adverse effect observed in 50% of the
215 population for a sub-lethal endpoint). Toxicity reference values were obtained from the

published literature (**Table 2**). Thus, a HQ is a screening tool that generates measures of levels of concern, though this method does not provide probability-based information of risk (Tannenbaum et al., 2003).

The equation for the acute hazard quotient is HQ = (MEC)/ (organism's EC_{50} or LC_{50} with 96-hours or less of exposure to the toxicant). An Affect Factor or Uncertainty Factor were not included in this equation. This quotient was derived for each of the 10 samples and compared to U.S. EPA's Level of Concern of 0.5 for aquatic animals (U.S.EPA, 2004; Gwinn et al., 2020), which were highlighted in red (**Table 2**).

A second method was used to calculate risk quotients that was based on the European Commission guidance regarding risk quotient (RQ) determination. The European Commission methodology has been adopted in the development of several ecological risk assessment guidelines (ECHA 2008; European Commission 1996, 2003; Environment Canada 2013; European medicines Agency 2006; Dussault et al., 2008; Hernando et al., 2006). With this method, the actual or predicted environmental concentration (MEC) is compared to a derived known or Predicted No-Effect Concentration (PNEC) which is derived by dividing the LC_{50}, EC_{50}, or NOEC by an uncertainty (or assessment) factor (UF). Thus, the RQ = (MEC)/(PNEC)(UF). For this RQ determination, an UF of 1000 was selected for the extrapolation of the $EC_{50,}$ LC_{50} or No Observable Effect Concentration (NOEC) values to estimate no-effect values (PNEC) (Chapman et al., 2009; Dussault et al., 2008; Means et al., 1993; Environment Canada, 2013). In cases where the NOEC was not known, but the Lowest Observable Effect Concentration (LOEC) was known, the LOEC was divided by two to calculate a predicted NOEC (ECHA, 2008). Toxicity reference values were obtained from the published literature (**Table 3**).

A number of endpoints not commonly used as regulatory toxicological endpoints are included in **Table 3**. However, all of these toxicity endpoints can be argued to reflect aspects necessary for population-level survival and reproductive fitness in real world situations (Goulson, 2013; Moore et al., 2004; Ruel and Ayres, 1999; Schafer et al., 1994).

The criteria for Levels of Concern for organisms in ecosystems for interpreting the RQ is based on a four-tier ranking system (European Commission 1996; Sanchez-Bayo et al. 2002; Hernando et al. 2006). Based on the American National Standards Institute recommendations for Hazard Communications, a color scheme is used for ease of visualization of the Levels of Concern for this methodology (**Table 3**). Red boxes indicate RQ values greater than 1, indicating an unacceptable risk requiring immediate action, and is the standard criteria for the Level of Concern within the European Commission framework. Orange boxes represent values between 0.5 and 1.0; a moderate concern of an acute impact. Yellow boxes represent values between 0.1 and 0.49, indicating a lower risk of impact. White boxes indicate no concern of danger.

Results

Measured Environmental Levels

Oxybenzone was measured from water column samples at each of 10 sampling locations within Hanauma Bay. Concentrations ranged from 136-27,880 ng/L as depicted in **Figure 1A** (nanograms per liter is equivalent to parts per trillion). Other benzophenones or benzotriazoles (UV blockers) also were measured in the bay. Benzophenone-1 was detected at a concentration of 21.94 ng/L from Site 9. Benzotriazole was detect in waters from Site 7 (16.48 ng/L), Site 8 (18.6 ng/L) and Site 9 (18.78 ng/L).

Beach sand collected from four beach-shower sites (**Figure 1B**) was analyzed for the presence of 10 UV filters (**Table 1**). Nine UV filters were detectable at each site, although several were below the limit of quantitation, depending on the site. Butyloctyl salicylate was not detected at any of the sites. The highest concentrations were found at Site 1 and the lowest at Site 4 with only four of the UV filters within quantitation limits. Octisalate was the highest measured UV filter among Sites 1-3, followed by homosalate. The concentrations of UV filters in **Table 1** are shown as uncorrected for recovery rates.

Sunscreen retention time in Hanauma Bay

Modelling scenarios for the retention time of sunscreen contaminants in Hanauma Bay are:

- Model scenario #1, Tidal Forcing = ~50 hours (**Figure 2**)
- Model scenario #2, Tidal and Oceanic (southward) Current Forcing = ~14 hours (**Figure 3**)
- Model scenario #3: Tidal and Shoreward Oceanic Current Forcing = ~ 41 hours (**Figure 4**)

Under normal conditions, when currents run to the south, contamination is flushed out of the Bay quickly - within 24 hrs. When currents run to the north (about 30% of the time), retention is much longer, assuming that there is no further interference from increasing number of bathers.

Hazard/Risk Analysis

Hazard and risk quotients are meant as a proactive means to determine if a chemical contaminant in a system is at a concentration that may pose a threat to a specific species population at that locality, or to the ecological integrity in that locality (U.S.EPA, 2004; Gwinn et al., 2020). It is also used to help define whether a system is polluted by a chemical; pollution being defined as causing or potentially causing a harmful effect (Connell & Miller, 1984). Calculated HQs for an acute exposure for each species and toxicity reference value are shown in **Table 2**. Based on the guidance by U.S. EPA (U.S.EPA, 2004; Gwinn et al., 2020), the most sensitive receptor represented in this dataset is *Pocillopora damicornis* coral cells exposed to oxybenzone during a 4 hour exposure involving light (LC_{50} = 8.0 µg/L) (**Table 2**). Based on the coral *in vitro* data, Sites 4 and 9 exhibited high risk to an acute exposure (**Table 2**). Based on the toxicity reference value for *Stylophora pistillata* planula exposed for 24 h with a day/night circadian cycle, Site 4 exhibited a high risk to acute exposure to oxybenzone at the measured concentration.

The RQ calculated using the European Commission (1996, 2003) method is argued to be a more rigorous and realistic estimation for risks than the U.S. EPA method for identifying threats to ecological integrity (Crane and Giddings, 2004).

Comparing coral cells exposed to oxybenzone in the light, the most threatened of the species was *P. damicornis*, while the relatively least-at-risk was *Porites astreoides*, and then

297 *Orbicella annularis* (**Table 3**). This is consistent with the predicted Species Sensitivity
298 distribution that branching morphologies are less stress tolerant than the "boulder" morphologies
299 (Downs et al., 2016). Calculated risk quotients indicate acute risk for all sites (**Table 3**). Based
300 on these data (**Figure 1A**), Sites 4 and 9 exhibited severe acute danger, while sites 3, 5, 7, 8 and
301 10 exhibited unacceptable danger for endangered animals and sites 3, 5, and 10 exhibited
302 increased risk for toxicity for non-endangered organisms. It should be noted that *P. damicornis* is
303 a species that should be found in abundance in the near-shore fringing reef area of Hanauma
304 Bay. Impromptu and formal surveys looking for *P. damicornis* indicate that this species may be
305 extinct within Hanauma Bay.

306 For coral and jellyfish planula, all the sites with the exception of Site 6 posed a serious
307 risk to planula viability based on the majority of the endpoints (**Table 3**). Planula deformity
308 LC_{50}s and EC_{50}s (8 hrs dark or 8 hrs light) showed the least risk across most sites. For coral
309 planula, DNA damage, zooxanthellae loss or damage (bleaching) precedes planula deformation –
310 coral experienced significant shifts in these biomarkers at the 8 hour of exposure mark when
311 compared to coral deformity. Coral morphological deformation occurs later in the pathological
312 timeline, and the risk assessment reflects this. Furthermore, it can be argued that these cellular
313 pathologies may predict the occurrence of the gross-morphological planula deformity (Moore et
314 al., 2004).

315 For non-cnidarian invertebrate species, risks were less pronounced though Sites 4 and 9
316 again contained concentrations of oxybenzone that posed the highest risks (**Table 3**). Sites 1,2,
317 and particularly 6 showed the least risk of adverse effects from oxybenzone exposure, although
318 all sites including these three exhibited some level of risk based on one or more endpoints.

Sites 4 and 9 posed the most threatening concentrations to every species of microalgae, as well as for all of the biomarker parameters (**Table 3**). Seagrass beds should populate sandy patches in the center and mouth of the bay, though they have been conspicuously absent or denuded for at least the past 20 years. There are no ecotoxicological studies for marine vascular plants, the closest surrogate for a vascular plant is cucumber (*Cucumis sativus*). Except for Site 6, all the sites posed a threat to photosynthetic and mitochondrial function, which can have an impact to above ground productivity and reproductive effort (**Table 3**). The toxicological sensitivity of microalgae to oxybenzone, and the risk condition for Hanauma Bay, calls into question the potential effects on the phytoplankton community structure.

Due to the relatively high sensitivity of fish toxicological parameters to oxybenzone, fish exhibited some of the highest levels of concern across most of the sampled area within Hanauma Bay (**Table 3**). *Brachydanio rerio* (96 hr LC_{50}) and *Danio rerio* (96 hr embryo LC_{50}) were the least at risk across the various sites. Markers for DNA damage were calculated to have enormously high-risk quotient values (e.g., *Poecilia reticulata*, **Table 3**).

Discussion

The over-arching question is whether sunscreen contamination poses a threat to the coral reef and seagrass ecosystems within Hanauma Bay, and whether anthropogenic activities such as sunbathing, swimming and snorkeling should be seen as a source of pollution. The second question we pose is whether beach showers can be a potential source of sunscreen contamination, since the waste waters are not collected by a municipal sewage system (untreated waste), but runs freely back into the bay. The third question we pose is, what is the potential retention time of a single day of contamination within Hanauma Bay? Recognition of sunscreen pollution means that resource managers and policy makers can confidently consider this a putative threat and consider options for mitigation. To begin to address the concern by managers of this "sunscreen sheen," it must first be determined if the composition in its entirety, or as individual components of a sunscreen mixture, pose a hazard to Hanauma's ecological integrity. One such probable singular chemical component of sunscreen pollution is oxybenzone.

Oxybenzone was detected in 100% of the water samples within Hanauma Bay. Concentration ranges were considerable, and were most likely a result of eddy formations between the reef and the shoreline, as well as tidal forcing.

This is the first study to demonstrate that beach showers near reefs may be a significant source of sunscreen chemical contamination into the environment. Sunscreen residue that is not released by swimmers during swimming can still contaminate Hanauma Bay via shower and rainfall run-off. Under the U.S. Clean Water Act, beach showers that are not connected to a municipal waste-water system can be classified as a "point source" of pollution for not just navigable waters, but for both State and U.S. federally protected waters (U.S. Clean Water Act, 2019).

Hawaii experiences a monsoonal-like climate, exhibiting a dry season and a wet season. During the dry season, sunscreen contaminants may accumulate to high concentrations in the sand within the shower plumes. The first rains of the rainy season may result in a high concentration pulse of sunscreen contaminants entering the receiving waters of Hanauma Bay. This pulse may pose an extreme and lethal hazard to the wildlife within Hanauma Bay. The dry season (May – August) sees less than 0.5 cm of precipitation per month within Hanauma. September is the beginning of the rainy season; November can see more than 1.25 cm of rain. This suggests that the highest concentrations of sunscreen contamination may occur in September, which is also the warmest time of the year and where coral bleaching events become observable. The period of sampling in November may exhibit the lowest level of sunscreen contamination, both as a condition of lower tourism intensity and increased flushing from peak precipitation.

Understanding the retention time of a pollutant allows for rigorous design and assessment of mitigation policies. Bay closures are becoming a resource management tool to relieve tourism pressures on targeted natural resources (County of Hawai'i, 2020; Koh and Fakfare, 2020; County of Hawai'i, 2021; Fox, 2021). How long should a bay be closed to ensure rapid dissipation of the pollution so as not to exceed hazard action levels? How many days should a bay be opened per week, and under what schedule that it may ensure a pollutant build-up does not occur (*e.g.*, open for one day, then closed the next two days)? Or should bays under high retention rates only be opened when oceanic flushing exceeds a minimal level of water exchange? Design and creation of marine protected areas might also require this information; reefs in bodies of water that have high retention rates may need more protection than more coastally exposed reefs. Finally, environmental impact assessments/statement regarding

residential and resort development need to consider the impact of increased visitor density from their businesses on the bay that are adjacent to their properties (U.S. EPA, 2011; Gross, 2018).

Coastal modeling of pollutants may also be necessary to determine other reef communities that are under risk of exposure. After exiting Hanauma Bay, dispersion of the pollutants was directly influenced by shelf circulation, ocean currents, and the interaction between the shallow shelf and deep ocean (Du et al., 2019). In addition, mesoscale eddies in the ocean can be influential in altering the water exchange between ocean and shelf as they move and dissipate. Could hydrophobic sunscreen pollutants be re-introduced into Hanauma Bay from these mesoscale behaviors? This complex situation needs more attention, as well as more comprehensive and sophisticated modeling and measurement attempts, along with a detailed understanding of oceanic current components in the area, which can be achieved from a data analysis of available global modelling over a longer period of time.

In this study, we compared the two major methodological approaches to risk assessment for contaminant data of oxybenzone collected in Hanauma Bay, Hawaii. The U.S. EPA Hazard quotient method is analogous to describing a chemical weapon detonation in a given area where it rapidly kills 50% of the population in the dispersion zone within a very short amount of time (e.g., 48-96 hours). It is the most simplistic of the deterministic models, and it inherently does not tell you about the consequence of the population that survives after an acute exposure, how long that population would survive after the initial exposure, its long-term impacts on the health of the acute-exposed population, or the impact of the exposure event when exposed to low concentrations to the toxicant (Somani & Romano, 2000; Volans & Karalliedde, 2002). The U.S. EPA method also says nothing about the threat of persistent, daily exposures to the toxicant at lower concentrations. Nor does it accommodate more recent social and scientific concerns of relying solely on animal-sacrifice toxicological models. But given these limitations, this hazard

assessment model demonstrated that some areas within Hanauma Bay, especially site 4, posed a serious threat to coral short-term survivability.

Site 4 of Hanauma Bay exhibited the greatest threat estimation (**Table 2**) using the US EPA method. It was the only site for coral planula, when exposed in the light, to have a hazard quotient value above 0.5. For the microalgae, *Isochrysis galbana*, the hazard quotient value was above 2, which is consistent with the fact the oxybenzone is particularly noxious to photosynthetic organisms. Oxybenzone is especially toxic to the electron transport chain of photosynthesis and oxidative phosphorylation in algae and plants, resulting in a reduction of growth and biomass (Mao et al., 2017; Zhang et al., 2019a; Zhang et al., 2019b). These high concentrations of oxybenzone and its effect on photosynthetic integrity may explain why there is an increased sensitivity of heat stress to induce coral bleaching. Oxybenzone can induce a bleaching pathology, and increase a coral's sensitivity to temperature stress, resulting in a bleaching response below the common bleaching temperature of two weeks at 30.3ºC (Downs et al., 2009; Downs et al., 2013; Downs et al., 2016; Wijgerde et al. 2020). Bleaching was observed in Hanauma Bay in 2015, even though temperatures never exceeded 29.8°C (Rodger et al., 2017; https://www.coralreefwatch.noaa.gov/). Bleaching was observed on reefs immediately adjacent to tourism-dense coastlines in 2019, but were relatively absent in more remote reefs or lightly visited reefs. These observations are consistent with the findings of Wijgerde et al. (2020) that oxybenzone exposure coupled with elevated temperatures increases the risk of coral to bleaching pathologies.

The model adopted by the European Commission is seen as the more relevant and accurate model that may explain the current condition of a geographic habitat that is contaminated with a personal care product chemical or pharmaceutical (Blasco et al., 2020). It uses uncertainty or assessment factors to calculate a more realistic account of a receptor's

toxicological sensitivities at different stages of its life history. Like the U.S. EPA method, it is limited by the temporal nature of the effect concentration data (e.g., 8 or 48 hours vs. 10 days), and thus can only calculate a risk assessment for the temporal time frame associated with the effect concentration data. Nonetheless, it provides a more relevant determination for the "danger" threshold of a contaminated site.

For *Stylophora* coral, all the sites had a risk quotient above 1, except Site 6, indicating that coral planulae are explicitly threatened with deformation (**Table 3**). For both deformity and mortality, light was an exacerbating factor that increased the threat of oxybenzone. This is consistent with oxybenzone and other benzophenone species acting as a photo-toxicant across a range of species (Downs et al., 2014; Downs et al., 2016; Zhang et al., 2021). Sites 4 and 9 exhibited risk quotient vales above 1 for all the species included in this assessment.

U.S. and European Union government regulatory agencies are advocating for the discontinuation of whole organism toxicity testing and shifting to New Approach Methods that utilize *in vitro* cell-toxicity testing for chemicals (Gwinn et al., 2020). Coral cells have been used to ascertain the toxicity of chemicals for over 10 years (Downs et al., 2010; Roger et al., 2021). Coral husbandry for ecotoxicological work is technically challenging and resource intensive. Coral cell toxicity testing shows remarkably similar exposure-concentration/response behavior as the intact colonial coral fragment (Downs et al., 2016). This is reflected in the pattern of risk quotients exhibited among the 10 sites between *Stylophora* coral cells in the light and dark versus *Stylophora* planula in the light and the dark (**Table 3**). *Pocillopora damicornis* is supposed to be an endemic species in Hanauma Bay, but is now possibly extinct (Dave Gulko, Hawaii Dept. Land & Natural Resources, personal communication). It is a much more stress-sensitive species compared to more massive-morphological coral species. The risk quotient for

Pocillopora was above one for all 10 sites, indicating that it would be unlikely to survive for long in this type of daily polluted environment.

Coral reef natural resources are under threat from intensive tourism. The most famous example is Maya Bay, Thailand. In 2018, Maya Bay saw more than 2.6 million visitors. The progression of ecological decay over the past 15 years was becoming impossible to disregard. In response, the Thai authorities shutdown Maya Bay for an indefinite amount of time to allow the habitats in Maya Bay to naturally recover, and to devise and implement a tourism management plan that would allow the sustainable interaction between tourists and biodiverse and ecological conservation (Koh and Fakfare, 2020). After six months without tourism, the recovery of wildlife was astonishingly observed (Dr. Thron Thamrongnawasawat, personal communication).

Hanauma Bay's waters are renowned for being grayishly turbid even on doldrum days, and swimmers exiting the water complain that they smell like a hodgepodge of "sunscreen fragrances." During the COVID-19 lockdown in 2020, no tourists or recreational visitors were allowed within Hanauma Bay for nine months (Caldwell, 2020). Reports indicate that water clarified to a point where the water returned to having a blue hue, and a significant increase in fish and invertebrate abundance were observed (Cruz, 2020). This expulsion of biodiversity during the tourism-visitation period of the past 30 years may be directly tied to sunscreen pollution within the bay. A recent study demonstrated that commercial sunscreens not only induced lethality at high concentrations in shrimp, but lower concentrations repelled the organism from the contaminated area, resulting in a *population immediate decline* phenomenon (Araujo et al., 2020). Maintenance of biodiversity and ecological community demographics may require banning all sunscreen products in the area until proven that the products do not result in repellence.

The focus of this study was on oxybenzone, but the presence of other sunscreen contaminants should be noted. The water analysis method focused almost exclusively on oxybenzone, but other contaminants were also observed, including benzophenone-1 (a metabolite of oxybenzone, and a cosmetic ingredient) and benzotriazole. Both compounds are renowned endocrine disruptors. Benzophenone-1 is much more toxic than the parent compound; it is 200-fold more estrogenic than oxybenzone (Gago-Ferrero et al., 2012). Regarding benzotriazoles' ecotoxicity, evidence indicates that these chemicals have endocrine disrupting properties, induces oxidative stress, hepatotoxicity and neurotoxicity in both freshwater and marine fish (Tangtian et al., 2012; Liang et al. 2014; Liang et al. 2016; Liang et al. 2017).

The survey of sunscreens in beach sand was based on a validated methodology that attains more than 85% recovery of each of the surveyed analytes, meaning that these concentrations are accurate, and that further studies should be conducted that focus on the distribution and impact of sunscreen compounds, not only avobenzone, octocrylene, octinoxate, octisalate and homosalate, but also other sunscreen ingredients such as parabens and phenoxyethanol. All of these UV filter compounds, including the carcinogen benzophenone, impart some level of endocrine disruption to animals, and begs the question of the endocrine disrupting potential of Hanauma Bay receiving waters, and how they may be impacting the Hanauma Bay's proximate habitats and endangered species. By logical progression, a pertinent question is whether the sullied waters of Hanauma Bay during intensive tourism periods poses a threat to public health, especially to pregnant persons and children (DiNardo and Downs 2019a; DiNardo and Downs 2019b).

DECLARATIONS

Ethical Approval: Not applicable.

Consent to Participate: Not applicable.

Consent for publication: Not applicable.

U.S. National Oceanic and Atmospheric Administration Disclaimer: The scientific results and conclusions, as well as any opinions expressed herein, are those of the author(s) and do not necessarily reflect the views of NOAA or the Department of Commerce. The mention of any commercial product is not meant as an endorsement by the Agency or Department.

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Availability of Data and Materials

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References

Almeida, S.D.S., Rocha, T.L., Qualhato, G., Oliveira, L.A.R., Amaral, C.L.D., Conceicao, E.C.D., Saboia-Morais, S.M.T., Bailao, E., 2019. Acute exposure to environmentally relevant concentrations of benzophenone-3 induced genotoxicity in *Poecilia reticulata*. Aquat Toxicol 216, 105293 DOI: 10.1016/j.aquatox.2019.105293.

Alonso, M.B., Feo, M.L., Corcellas, C., Gago-Ferrero, P., Bertozzi, C.P., Marigo, J., Flach, L., Meirelles, A.C., Carvalho, V.L., Azevedo, A.F., Torres, J.P., Lailson-Brito, J., Malm, O., Diaz-Cruz, M.S., Eljarrat, E., Barcelo, D., 2015. Toxic heritage: Maternal transfer of pyrethroid insecticides and sunscreen agents in dolphins from Brazil. Environ Pollut 207, 391-402 DOI: 10.1016/j.envpol.2015.09.039.

Araujo, C.V.M., Rodriguez-Romero, A., Fernandez, M., Sparaventi, E., Medina, M.M., Tovar-Sanchez, A., 2020. Repellency and mortality effects of sunscreens on the shrimp *Palaemon varians*: Toxicity dependent on exposure method. Chemosphere 257, 127190 DOI: 10.1016/j.chemosphere.2020.127190.

Australian Government, 2013. NICNAS Cosmetics Guidelines. Department of Health. Archived from the original.

Blasco, J., Trombini, C., Sendra, M., Araujo, C.V.M., 2020. Environmental Risk Assessment of Sunscreens. Sunscreens in Coastal Ecosystems, pp. 163-184.

Blitz, J.B., Norton, S.A., 2008. Possible environmental effects of sunscreen run-off. J Am Acad Dermatol 59, 898-898 DOI: 10.1016/j.jaad.2008.06.013.

555

556 Blüthgen, N., Zucchi, S., Fent, K., 2012. Effects of the UV filter benzophenone-3 (oxybenzone)
557 at low concentrations in zebrafish (*Danio rerio*). Toxicol Appl Pharm 263, 184-194 DOI:
558 http://dx.doi.org/10.1016/j.taap.2012.06.008.

559

560 Booth, H.H., Manning, M.M., 2017. Assessing the sunscreen sheen: determining the presence of
561 organic UV filters from four sites at the Hanauma Bay Marine Life Conservation District. Poster
562 29292. Association for the Sciences of Limnology & Oceanography (ASLO), Honolulu, Hawai'i.

563

564 Bošnjak, I., Pleic, I.L., Borra, M., Mladineo, I., 2013. Quantification and in situ localisation of
565 abcb1 and abcc9genes in toxicant-exposed sea urchin embryos. Environ Sci Pollut Res Int 20,
566 8600-8611 DOI: 10.1007/s11356-013-1819-2.

567

568 Boyd, A., Stewart, C.B., Philibert, D.A., How, Z.T., El-Din, M.G., Tierney, K.B., Blewett, T.A.,
569 2021. A burning issue: The effect of organic ultraviolet filter exposure on the behaviour and
570 physiology of *Daphnia magna*. Sci Total Environ 750, 141707 DOI:
571 10.1016/j.scitotenv.2020.141707.

572

573 Caldwell, K.W., 2020. Supplemental Proclamation of Emergency or Disaster (COVID-19 [Novel
574 Coronavirus]). Office of the Mayor, City and County of Honolulu, Hawaii.
575 https://www.honolulu.gov/rep/site/may/may_docs/Supplemental_Proc_of_Emergency_or_Disast
576 er_COVID19_03182020.pdf accessed 17 July 2021

577

578 Chapman PM, Fairbrother A, Brown D (1998) A critical evaluation of safety (uncertainty)
579 factors for ecological risk assessment. Environmental Toxicology and Chemistry 17:99-108.
580
581 Chaves Lopes, F., Rosa de Castro, M., Caldas Barbosa, S., Primel, E.G., de Martinez Gaspar
582 Martins, C., 2020. Effect of the UV filter, benzophenone-3, on biomarkers of the yellow clam
583 (*Amarilladesma mactroides*) under different pH conditions. Mar Pollut Bull 158, 111401 DOI:
584 10.1016/j.marpolbul.2020.111401.
585
586 Chen, T.H., Wu, Y.T., Ding, W.H., 2016. UV-filter benzophenone-3 inhibits agonistic behavior
587 in male Siamese fighting fish (*Betta splendens*). Ecotoxicology 25, 302-309 DOI:
588 10.1007/s10646-015-1588-4.
589 Cocci, P., Mosconi, G., Palermo, F.A., 2020. Sunscreen active ingredients in loggerhead turtles
590 (*Caretta caretta*) and their relation to molecular markers of inflammation, oxidative stress and
591 hormonal activity in wild populations. Mar Pollut Bull 153, 111012 DOI:
592 10.1016/j.marpolbul.2020.111012.
593
594 Connell, D.W., Miller, G.J., 1984. *Chemistry and Ecotoxicology of Pollution*. John Wiley &
595 Sons Inc., New York.
596
597 Coronado, M., De Haro, H., Deng, X., Rempel, M.A., Lavado, R., Schlenk, D., 2008. Estrogenic
598 activity and reproductive effects of the UV-filter oxybenzone (2-hydroxy-4-methoxyphenyl-
599 methanone) in fish. Aquat Toxicol 90, 182-187 DOI: 10.1016/j.aquatox.2008.08.018.

County of Hawai'i, 2020. Rest and Restoration for Cauliflower Coral in Kahalu'u Bay. Department of Land and Natural Resources, Honolulu, Hawai'i https://dlnr.hawaii.gov/blog/2020/05/07/nr20-059/ accessed 17 July 2021

County of Hawai'i, 2021. Coral Spawning Prompts Temporary Closures at Waialea Bay Marine Life Conservation District. Department of Land and Natural Resources, Honolulu, Hawai'i. https://dlnr.hawaii.gov/dsp/announcements/coral-spawning-prompts-temporary-closures-at-waialea-bay-marine-life-conservation-district/ accessed 17 July 2021

Crane, M., Giddings, J.M., 2004. "Ecologically Acceptable Concentrations" when assessing the environmental risks of pesticides under European Directive 91/414/EEC. Hum Ecol Risk Assess 10, 733-747 DOI: 10.1080/10807030490484237.

Cruz, C., 2020. The Conversation. What's Happened at Hanauma Bay Since the COVID-19 Crisis. Hawai'i Public Radio, Hawai'i.

Danovaro, R., Bongiorni, L., Corinaldesi, C., Giovannelli, D., Damiani, E., Astolfi, P., Greci, L., Pusceddu, A., 2008. Sunscreens cause coral bleaching by promoting viral infections. Environ Health Perspect 116, 441-447 DOI: 10.1289/ehp.10966.

Diaz-Cruz, M.S., Barceló, D., 2015. *Personal Care Products in the Aquatic Environment*, 1st ed. Springer International Publishing, Switzerland.

DiNardo, J.C., Downs, C.A., 2019. Can oxybenzone cause Hirschsprung's disease? Reprod Toxicol DOI: 10.1016/j.reprotox.2019.02.014.

DiNardo, J.C., Downs, C.A., 2020. Should a toxicological risk assessment of ubiquitous chemicals be done using data from only one source of exposure? Open Access Journal of Toxicology 4, 555633 DOI: 10.19080/OAJT.2020.04.555633.

Downs, C.A., Fauth, J.E., Downs, V.D., Ostrander, G.K., 2010. *In vitro* cell-toxicity screening as an alternative animal model for coral toxicology: effects of heat stress, sulfide, rotenone, cyanide, and cuprous oxide on cell viability and mitochondrial function. Ecotoxicology 19, 171-184 DOI: 10.1007/s10646-009-0403-5.

Downs, C.A., Kramarsky-Winter, E., Fauth, J.E., Segal, R., Bronstein, O., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Kushmaro, A., Loya, Y., 2014. Toxicological effects of the sunscreen UV filter, benzophenone-2, on planulae and in vitro cells of the coral, *Stylophora pistillata.* Ecotoxicology 23, 175-191 DOI: 10.1007/s10646-013-1161-y.

Downs, C.A., Kramarsky-Winter, E., Martinez, J., Kushmaro, A., Woodley, C.M., Loya, Y., Ostrander, G.K., 2009. Symbiophagy as a cellular mechanism of coral bleaching. Autophagy 5, 211-216.

Downs, C.A., Kramarsky-Winter, E., Segal, R., Fauth, J., Knutson, S., Bronstein, O., Ciner, F.R., Jeger, R., Lichtenfeld, Y., Woodley, C.M., Pennington, P., Cadenas, K., Kushmaro, A., Loya, Y., 2016. Toxicopathological effects of the sunscreen UV filter, oxybenzone (benzophenone-3), on

coral planulae and cultured primary cells and its environmental contamination in Hawaii and the U.S. Virgin Islands. Arch Environ Contam Toxicol 70, 265-288 DOI: 10.1007/s00244-015-0227-7.

Downs, C.A., McDougall, K.E., Woodley, C.M., Fauth, J.E., Richmond, R.H., Kushmaro, A., Gibb, S.W., Loya, Y., Ostrander, G.K., Kramarsky-Winter, E., 2013. Heat-stress and light-stress induce different cellular pathologies in the symbiotic dinoflagellate during coral bleaching. PLoS One 8, e77173 DOI: 10.1371/journal.pone.0077173.

Du, Y., Wang, W.Q., Pei, Z.T., Ahmad, F., Xu, R.R., Zhang, Y.M., Sun, L.W., 2017. Acute toxicity and ecological risk assessment of benzophenone-3 (BP-3) and benzophenone-4 (BP-4) in ultraviolet (UV)-filters. Int J Environ Res Public Health 14 DOI: 10.3390/ijerph14111414.

Du, J., Qv, M., Li, K., Yin, X., Meng, F., Yang, J., Ma, C., 2019. Impacts of benzophenone-type UV filters on cladoceran *Daphnia carinata*. Limnology 20, 173-179 DOI: 10.1007/s10201-018-0563-1.

Dussault EB, Balakrishnan VK, Sverko E, Solomon KR, Sibley PK. (2008) Toxicity of human pharmaceuticals and personal care products to benthic invertebrates. *Environmental Toxicology and Chemistry*. 27: 425-432.

ECHA, 2008. Chapter R.10: Characterization of dose [concentration]-response for environment. Guidance on Information Requirements and Chemical Safety Assessment. European Chemicals Agency.

https://echa.europa.eu/documents/10162/13632/information_requirements_r10_en.pdf/bb902be7-a503-4ab7-9036-d866b8ddce69 accessed 17 July 2021

European Commission, 2003a. Technical Guidance Document on Risk Assessment Part I. EUR 20418 EN/1. European Chemicals Bureau, Ispra, Italy. https://echa.europa.eu/documents/10162/16960216/tgdpart1_2ed_en.pdf accessed 17 July 2021

European Commission, 2003b. Technical Guidance Document on Risk Assessment Part II. EUR 20418 EN/2 European Chemical Bureau, Ispra, Italy. https://op.europa.eu/en/publication-detail/-/publication/9aebb292-39c5-4b9c-b4cb-97fb02d9bea2/language-en/format-PDF/source-search accessed 17 July 2021

European Commission, 2003c. Technical Guidance Document on Risk Assessment Part III. EUR 20418 EN/3. European Chemical Bureau, Ispra, Italy. https://echa.europa.eu/documents/10162/16960216/tgdpart3_2ed_en.pdf accessed 17 July 2021

European Commission, 2019. 2-hydroxy-4-methoxybenzophenone/oxybenzone. Cosmetic Ingredient Database (Cosing). https://ec.europa.eu/growth/tools-databases/cosing/pdf/COSING_Annex%20VI_v2.pdf accessed 17 July 2021

European Medicines Agency (EMEA). (2006) Guideline on the Environmental Risk Assessment of Medicinal Products for Human Use. http://www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2009/10/WC500003978.pdf (Accessed 8-5-20)

European Union, 2009. Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. https://ec.europa.eu/health/sites/default/files/endocrine_disruptors/docs/cosmetic_1223_2009_regulation_en.pdf accessed 17 July 2021

Fent, K., Zenker, A., Rapp, M., 2010a. Widespread occurrence of estrogenic UV-filters in aquatic ecosystems in Switzerland. Environ Pollut 158, 1817-1824 DOI: 10.1016/j.envpol.2009.11.005.

Fitt, W.K., Hofmann, D.K., 2020. The effects of the UV-blocker oxybenzone (benzophenone-3) on planulae swimming and metamorphosis of the scyphozoans *Cassiopea xamachana* and *Cassiopea frondosa*. Oceans 1, 174-180 DOI: 10.3390/oceans1040013.

Fox, C.T., 2021. Kahalu'u Beach Park in Kona Closed for Coral Spawning. *Hawai'i Magazine*. aio Media Group, Honolulu, Hawai'i.

Gago-Ferrero, P., Badia-Fabregat, M., Olivares, A., Pina, B., Blanquez, P., Vicent, T., Caminal, G., Diaz-Cruz, M.S., Barceló, D., 2012. Evaluation of fungal- and photo-degradation as potential treatments for the removal of sunscreens BP3 and BP1. Sci Total Environ 427-428, 355-363 DOI: 10.1016/j.scitotenv.2012.03.089.

Goulson, D., Kleijn, D., 2013. An overview of the environmental risks posed by neonicotinoid insecticides. J Appl Ecol 50, 977-987 DOI: 10.1111/1365-2664.12111.

Gross, M., 2018. Global tourism's growing footprint. Curr Biol 28, R963-R965 DOI: 10.1016/j.cub.2018.08.049.

Gwinn, M., Cowden, J., Lambert, J.C., Lowit, A., Wetmore, B.A., Scarano, L., Schappelle, S., Thomas, R.S., Burman, E., 2020. Alternative Toxicity Testing Report to Congress. U. S. Environmental Protection Agency, Washington, D.C. DOI: 10.23645/epacomptox.12283958.v4

He, T., Tsui, M.M.P., Tan, C.J., Ma, C.Y., Yiu, S.K.F., Wang, L.H., Chen, T.H., Fan, T.Y., Lam, P.K.S., Murphy, M.B., 2019a. Toxicological effects of two organic ultraviolet filters and a related commercial sunscreen product in adult corals. Environ Pollut 245, 462-471 DOI: 10.1016/j.envpol.2018.11.029.

He, T., Tsui, M.M.P., Tan, C.J., Ng, K.Y., Guo, F.W., Wang, L.H., Chen, T.H., Fan, T.Y., Lam, P.K.S., Murphy, M.B., 2019b. Comparative toxicities of four benzophenone ultraviolet filters to two life stages of two coral species. Sci Total Environ 651, 2391-2399 DOI: 10.1016/j.scitotenv.2018.10.148.

Hernando MD, Mezcua M. Fernandex-Alba AR, Barcelo D. (2006) Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta*. 69: 334-342

Japan, 2000. Standards for Cosmetics. Ministry of Health and Welfare, Tokyo. https://www.mhlw.go.jp/file/06-Seisakujouhou-11120000-Iyakushokuhinkyoku/0000032704.pdf accessed 17 July 2021

743 Jang, G.H., Park, C.B., Kang, B.J., Kim, Y.J., Lee, K.H., 2016. Sequential assessment via
744 daphnia and zebrafish for systematic toxicity screening of heterogeneous substances. Environ
745 Pollut 216, 292-303 DOI: 10.1016/j.envpol.2016.06.001.

746 Jiang, C., Liu, Y., Long, Y., Wu, C., 2017. Estimation of residence time and transport trajectory
747 in Tieshangang Bay, China. Water 9 DOI: 10.3390/w9050321.
748
749 Kinnberg, K.L., Petersen, G.I., Albrektsen, M., Minghlani, M., Awad, S.M., Holbech, B.F.,
750 Green, J.W., Bjerregaard, P., Holbech, H., 2015. Endocrine-disrupting effect of the ultraviolet
751 filter benzophenone-3 in zebrafish, *Danio rerio*. Environ Toxicol Chem 34, 2833-2840.

752 Koh, E., Fakfare, P., 2020. Overcoming "over-tourism": the closure of Maya Bay. J Tour Cities
753 6, 279-296 DOI: https://doi.org/10.1108/IJTC-02-2019-0023.
754
755 Kopp, R., Martinez, I.O., Legradi, J., Legler, J., 2017. Exposure to endocrine disrupting
756 chemicals perturbs lipid metabolism and circadian rhythms. J Environ Sci (China) 62, 133-137
757 DOI: 10.1016/j.jes.2017.10.013.

758 Kunz, P.Y., Fent, K., 2006. Multiple hormonal activities of UV filters and comparison of in vivo
759 and in vitro estrogenic activity of ethyl-4-aminobenzoate in fish. Aquat Toxicol 79, 305-324
760 DOI: 10.1016/j.aquatox.2006.06.016.
761
762 Kunz, P.Y., Galicia, H.F., Fent, K., 2006. Comparison of *in vitro* and *in vivo* estrogenic activity
763 of UV filters in fish. Toxicol Sci 90, 349-361 DOI: 10.1093/toxsci/kfj082.
764

765 Lambrechts, J., Hanert, E., Deleersnijder, E., Bernard, P.-E., Legat, V., Remacle, J.- F., *et al.*,
766 2008. A multi-scale model of the hydrodynamics of the whole Great Barrier Reef. *Estuar. Coast.*
767 *Shelf Sci.* 79, 143–151.
768
769 Lee, S.-H., Xiong, J.-Q., Ru, S., Patil, S.M., Kurade, M.B., Govindwar, S.P., Oh, S.-E., Jeon, B.-
770 H., 2020. Toxicity of benzophenone-3 and its biodegradation in a freshwater microalga
771 *Scenedesmus obliquus*. J Hazard Mater, 122149 DOI: 10.1016/j.jhazmat.2020.122149.
772
773 Li, M.-H., 2012. Acute toxicity of benzophenone-type UV filters and paraben preservatives to
774 freshwater planarian, *Dugesia japonica*. Toxicol Environ Chem 94, 566-573 DOI:
775 10.1080/02772248.2012.655695.
776
777 Liang, X., Martyniuk, C.J., Zha, J., Wang, Z., 2016. Brain quantitative proteomic responses
778 reveal new insight of benzotriazole neurotoxicity in female Chinese rare minnow (*Gobiocypris*
779 *rarus*). Aquat Toxicol 181, 67-75 DOI: 10.1016/j.aquatox.2016.10.030.
780
781 Liang, X., Wang, M., Chen, X., Zha, J., Chen, H., Zhu, L., Wang, Z., 2014. Endocrine disrupting
782 effects of benzotriazole in rare minnow (*Gobiocypris rarus*) in a sex-dependent manner.
783 Chemosphere 112, 154-162 DOI: 10.1016/j.chemosphere.2014.03.106.
784
785 Liang, X., Zha, J., Martyniuk, C.J., Wang, Z., Zhao, J., 2017. Histopathological and proteomic
786 responses in male Chinese rare minnow (*Gobiocypris rarus*) indicate hepatotoxicity following
787 benzotriazole exposure. Environ Pollut 229, 459-469 DOI: 10.1016/j.envpol.2017.06.013.
788

789 Mak, J., Moncur, J.T., 1995. Sustainable tourism development: managing Hawai'i's "unique"
790 touristic resource --Hanauma Bay. J. Travel Res. 33, 51-57.
791
792 Mao, F., He, Y., Kushmaro, A., Gin, K.Y., 2017. Effects of benzophenone-3 on the green alga
793 *Chlamydomonas reinhardtii* and the cyanobacterium *Microcystis aeruginosa*. Aquat Toxicol
794 193, 1-8 DOI: 10.1016/j.aquatox.2017.09.029.
795
796 Mao, F., He, Y., Gin, K.Y., 2020. Antioxidant responses in cyanobacterium *Microcystis*
797 *aeruginosa* caused by two commonly used UV filters, benzophenone-1 and benzophenone-3, at
798 environmentally relevant concentrations. J Hazard Mater 396, 122587 DOI:
799 10.1016/j.jhazmat.2020.122587.
800 Meng, Q., Yeung, K., Kwok, M.L., Chung, C.T., Hu, X.L., Chan, K.M., 2020. Toxic effects and
801 transcriptome analyses of zebrafish (*Danio rerio*) larvae exposed to benzophenones. Environ
802 Pollut 265, 114857 DOI: 10.1016/j.envpol.2020.114857.
803 Molins-Delgado, D., Gago-Ferrero, P., Diaz-Cruz, M.S., Barcelo, D., 2016. Single and joint
804 ecotoxicity data estimation of organic UV filters and nanomaterials toward selected aquatic
805 organisms. Urban groundwater risk assessment. Environ Res 145, 126-134 DOI:
806 10.1016/j.envres.2015.11.026.
807
808 Moore, M.N., Depledge, M.H., Readman, J.W., Paul Leonard, D.R., 2004. An integrated
809 biomarker-based strategy for ecotoxicological evaluation of risk in environmental management.
810 Mutat Res 552, 247-268 DOI: 10.1016/j.mrfmmm.2004.06.028.
811

812 Na, J., Song, J., Achar, J.C., Jung, J., 2021. Synergistic effect of microplastic fragments and
813 benzophenone-3 additives on lethal and sublethal *Daphnia magna* toxicity. J Hazard Mater 402
814 DOI: 10.1016/j.jhazmat.2020.123845.

815 National Research Council (NRC) 1983. Risk Assessment in the Federal Government: Managing
816 the Process. National Academies Press, Washington, D.C. https://www.nap.edu/catalog/366/risk-
817 assessment-in-the-federal-government-managing-the-process accessed 17 July 2021
818
819 National Research Council (NRC) 2009. Science and Decisions: Advancing Risk Assessment.
820 National Academies Press, Washington, D.C. https://www.nap.edu/catalog/12209/science-and-
821 decisions-advancing-risk-assessment accessed 17 July 2021
822
823 O'Donovan, S., Mestre, N.C., Abel, S., Fonseca, T.G., Carteny, C.C., Willems, T., Prinsen, E.,
824 Cormier, B., Keiter, S.S., Bebianno, M.J., 2020. Effects of the UV filter, oxybenzone, adsorbed
825 to microplastics in the clam *Scrobicularia plana*. Sci Total Environ 733, 139102 DOI:
826 10.1016/j.scitotenv.2020.139102.
827
828 Ozaez, I., Martinez-Guitarte, J.L., Morcillo, G., 2014. The UV filter benzophenone 3 (BP-3)
829 activates hormonal genes mimicking the action of ecdysone and alters embryo development in
830 the insect *Chironomus riparius* (Diptera). Environ Pollut 192, 19-26 DOI:
831 10.1016/j.envpol.2014.04.038.
832
833 Pablos, M.V., Garcia-Hortiguela, P., Fernandez, C., 2015. Acute and chronic toxicity of
834 emerging contaminants, alone or in combination, in *Chlorella vulgaris* and *Daphnia magna*.
835 Environ Sci Pollut Res Int 22, 5417-5424 DOI: 10.1007/s11356-015-4119-1.

Paredes, E., Perez, S., Rodil, R., Quintana, J.B., Beiras, R., 2014. Ecotoxicological evaluation of four UV filters using marine organisms from different trophic levels *Isochrysis galbana*, *Mytilus galloprovincialis*, *Paracentrotus lividus*, and *Siriella armata*. Chemosphere 104, 44-50 DOI: 10.1016/j.chemosphere.2013.10.053.

Petersen, K., Heiaas, H.H., Tollefsen, K.E., 2014. Combined effects of pharmaceuticals, personal care products, biocides and organic contaminants on the growth of *Skeletonema pseudocostatum*. Aquat Toxicol 150, 45-54 DOI: 10.1016/j.aquatox.2014.02.013.

Rodgers, K.S., Bahr, K.D., Jokiel, P.L., Richards Dona, A., 2017. Patterns of bleaching and mortality following widespread warming events in 2014 and 2015 at the Hanauma Bay Nature Preserve, Hawai'i. PeerJ 5, e3355 DOI: 10.7717/peerj.3355.

Rodrigues, A.M.S., Lebaron, P., Downs, C.A., Stien, D., 2021. Optimization method for quantification of sunscreen organic ultraviolet filters in coastal sands. J Sep Sci DOI: 10.1002/jssc.202100400.

Rodriguez-Fuentes, G., Sandoval-Gio, J.J., Arroyo-Silva, A., Norena-Barroso, E., Escalante-Herrera, K.S., Olvera-Espinosa, F., 2015. Evaluation of the estrogenic and oxidative stress effects of the UV filter 3-benzophenone in zebrafish (*Danio rerio*) eleuthero-embryos. Ecotoxicol Environ Saf 115, 14-18 DOI: 10.1016/j.ecoenv.2015.01.033.

Roger, L.M., Reich, H.G., Lawrence, E., Li, S., Vizgaudis, W., Brenner, N., Kumar, L., Klein-Seetharaman, J., Yang, J., Putnam, H.M., Lewinski, N.A., 2021. Applying model approaches in

860 non-model systems: A review and case study on coral cell culture. PLoS One 16, e0248953 DOI:
861 10.1371/journal.pone.0248953.
862
863 Ruel, J., Ayres, M., 1999. Jensen's inequality predicts effects of environmental variation. Trends
864 Ecol Evol 14, 361-366.
865
866 Sanchez-Bayo F., Baskaran, S., Kennedy, I.R., 2002. Ecological relative risk (EcoRR): another
867 approach for risk assessment of pesticides ina griculture. Agric Ecosyst and Environ 91,37-57.
868
869 Schafer, H., Hettler, H., Fritsche, U., Pitzen, G., Roderer, G., Wenzel, A., 1994. Biotests using
870 unicellular algae and ciliates for predicting long-term effects of toxicants. Ecotox Environ Safe
871 27, 64-81.
872
873 Schlumpf, M., Cotton, B., Conscience, M., Haller, V., Steinmann, B., Lichtensteiger, W., 2001.
874 *In vitro* and *in vivo* estrogenicity of UV sunscreens. Environ Health Perspect 109, 239-244.
875
876 Schlumpf, M., Schmid, P., Durrer, S., Conscience, M., Maerkel, K., Henseler, M., Gruetter, M.,
877 Herzog, I., Reolon, S., Ceccatelli, R., Faass, O., Stutz, E., Jarry, H., Wuttke, W., Lichtensteiger,
878 W., 2004. Endocrine activity and developmental toxicity of cosmetic UV filters--an update.
879 Toxicology 205, 113-122 DOI: 10.1016/j.tox.2004.06.043.
880
881 Schreurs, R., Lanser, P., Seinen, W., van der Burg, B., 2002. Estrogenic activity of UV filters
882 determined by an in vitro reporter gene assay and an in vivo transgenic zebrafish assay. Arch
883 Toxicol 76, 257-261 DOI: 10.1007/s00204-002-0348-4.

884

885 Seoane, M., Cid, A., Herrero, C., Esperanza, M., 2020. Comparative acute toxicity of
886 benzophenone derivatives and bisphenol analogues in the Asian clam *Corbicula fluminea*.
887 Ecotoxicology DOI: 10.1007/s10646-020-02299-w.

888

889 Sieratowicz, A., Kaiser, D., Behr, M., Oetken, M., Oehlmann, J., 2011. Acute and chronic
890 toxicity of four frequently used UV filter substances for *Desmodesmus subspicatus* and *Daphnia*
891 *magna*. J Environ Sci Health A Tox Hazard Subst Environ Eng 46, 1311-1319 DOI:
892 10.1080/10934529.2011.602936.

893

894 Somani, S.M., Romano, J.A.J. (eds), 2000. Chemical Warfare Agents: Toxicity at Low Levels.
895 CRC Press, Boca Raton.

896

897 Stien, D., Suzuki, M., Rodrigues, A.M.S., Yvin, M., Clergeaud, F., Thorel, E., Lebaron, P., 2020.
898 A unique approach to monitor stress in coral exposed to emerging pollutants. Sci Rep 10, 9601
899 DOI: 10.1038/s41598-020-66117-3.

900

901 Sun, H.Q., Du, Y., Zhang, Z.Y., Jiang, W.J., Guo, Y.M., Lu, X.W., Zhang, Y.M., Sun, L.W.,
902 2016. Acute toxicity and ecological risk assessment of benzophenone and N,N-Diethyl-3
903 Methylbenzamide in personal care products. Int J Environ Res Public Health 13 DOI:
904 10.3390/ijerph13090925.

905

Tangtian, H., Bo, L., Wenhua, L., Shin, P.K., Wu, R.S., 2012. Estrogenic potential of benzotriazole on marine medaka (*Oryzias melastigma*). Ecotoxicol Environ Saf 80, 327-332 DOI: 10.1016/j.ecoenv.2012.03.020.

Tannenbaum, L.V., Johnson, M.S., Bazar, M., 2003. Application of the hazard quotient method in remedial decisions: A comparison of human and ecological risk assessments. Hum Ecol Risk Assess 9, 387-401.

Tao, J., Bai, C., Chen, Y., Zhou, H., Liu, Y., Shi, Q., Pan, W., Dong, H., Li, L., Xu, H., Tanguay, R., Huang, C., Dong, Q., 2020. Environmental relevant concentrations of benzophenone-3 induced developmental neurotoxicity in zebrafish. Sci Total Environ 721, 137686 DOI: 10.1016/j.scitotenv.2020.137686.

Teoh, M.-L., Sanusi, N.S., Wong, C.-Y., Beardall, J., 2020. Effects of the sunscreen ultraviolet filter, oxybenzone, on green microalgae. Adv Polar Sci 31, 112-123 DOI: 10.13679/j.advps.2019.0041.

Thomas, C. J., Bridge, T. C., Figueiredo, J., Deleersnijder, E., and Hanert, E., 2015. Connectivity between submerged and near-sea-surface coral reefs: can submerged reef populations act as refuges? Biodiversity Distrib, https://doi.org/10.1111/ddi.12360.

Thomas, Christopher J., Lambrechts, Jonathan, Wolanski, Eric, Traag, Vincent A., Blondel, Vincent D., Deleersnijder, Eric, Hanert, Emmanuel, 2014. Numerical modelling and graph

theory tools to study ecological connectivity in the Great Barrier Reef. *Ecological Modelling*, Elsevier, Vol. 272(C), pp. 160-174.

Thorel, E., Clergeaud, F., Jaugeon, L., Rodrigues, A.M.S., Lucas, J., Stien, D., Lebaron, P., 2020. Effect of 10 UV filters on the brine shrimp *Artemia salina* and the marine microalgae *Tetraselmis* sp. Toxics, p. 29. DOI: 10.3390/toxics8020029

Tsanis, I., Wu, J., Shen, H., Valeo, C., 2006. Environmental Hydraulics. Hydrodynamic and Pollutant Transport Models of Lakes and Coastal Waters, 1st ed. Elsevier Science.

U.S. Clean Water Act, 2019. Clean Water Act Section 502: General Definitions. U. S. Environmental Protection Agency. https://www.epa.gov/cwa-404/clean-water-act-section-502-general-definitions accessed 17 July 2021

U.S. EPA, 1992. Guidelines for Exposure Assessment. EPA/600/Z-92/001 Federal Register, 57, 22888-22938. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=15263 accessed 17 July 2021

U.S. EPA, 1998. Guidelines for Ecological Risk Assessment. EPA/630/R-95/002F Federal Register, 63, 26846-26924. https://www.epa.gov/sites/default/files/2014-11/documents/eco_risk_assessment1998.pdf accessed 17 July 2021

U.S. EPA, 2004. Overview of the Ecological Risk Assessment Process Endangered and Threatened Species Effects Determination. Office of Pesticide Programs, U.S. Environmental Protection Agency. Washington, D.C., p. 92. https://www.epa.gov/sites/default/files/2014-11/documents/ecorisk-overview.pdf accessed 17 July 2021

U.S. EPA, 2011. EIA Technical Review Guidelines: Tourism-Related Projects. U.S. Environmental Protection Agency. Washington, D.C. https://www.epa.gov/sites/default/files/2014-04/documents/tourismvol1.pdf accessed 17 July 2021

U.S. EPA, 2018. National Air Toxics Assessment Technical Supporting Document. Office of Air Quality Planning and Standards, Research Triangle Park North Carolina 27711. https://www.epa.gov/national-air-toxics-assessment/2014-nata-technical-support-document accessed 17 July 2021

U.S. FDA, 1978. Sunscreen drug products for over-the-counter-human use. Federal Register 43, 38206-38269.

U.S. FDA, 2019. Sunscreen drug products for over-the-counter human use. Federal Register 84, 6204-6275.

Volans, G.N., Karalliedde, L., 2002. Long-term effects of chemical weapons. The Lancet 360, s35-s36 DOI: 10.1016/s0140-6736(02)11813-7.

975

976 Wijgerde, T., van Ballegooijen, M., Nijland, R., van der Loos, L., Kwadijk, C., Osinga, R.,
977 Murk, A., Slijkerman, D., 2020. Adding insult to injury: Effects of chronic oxybenzone exposure
978 and elevated temperature on two reef-building corals. Sci Total Environ 733, 139030 DOI:
979 10.1016/j.scitotenv.2020.139030.

980

981 Zhang, P., Lu, G., Liu, J., Yan, Z., Wang, Y., 2020. Toxicological responses of *Carassius*
982 *auratus* induced by benzophenone-3 exposure and the association with alteration of gut
983 microbiota. Sci Total Environ 747, 141255 DOI: 10.1016/j.scitotenv.2020.141255.

984

985 Zhang, Y., Shah, P., Wu, F., Liu, P., You, J., Goss, G., 2021. Potentiation of lethal and sub-lethal
986 effects of benzophenone and oxybenzone by UV light in zebrafish embryos. Aquat Toxicol 235,
987 105835 DOI: 10.1016/j.aquatox.2021.105835.

988

989 Zhong, X., Downs, C.A., Che, X., Zhang, Z., Li, Y., Liu, B., Li, Q., Li, Y., Gao, H., 2019a. The
990 toxicological effects of oxybenzone, an active ingredient in suncream personal care products, on
991 prokaryotic alga *Arthrospira* sp. and eukaryotic alga *Chlorella* sp. Aquat Toxicol 216, 105295
992 DOI: 10.1016/j.aquatox.2019.105295.

993

994 Zhong, X., Li, Y., Che, X., Zhang, Z., Li, Y., Liu, B., Li, Q., Gao, H., 2019b. Significant
995 inhibition of photosynthesis and respiration in leaves of *Cucumis sativus* L. by oxybenzone, an
996 active ingredient in sunscreen. Chemosphere 219, 456-462 DOI:
997 10.1016/j.chemosphere.2018.12.019.

998

Zhong, X., Downs, C.A., Li, Y., Zhang, Z., Li, Y., Liu, B., Gao, H., Li, Q., 2020. Comparison of toxicological effects of oxybenzone, avobenzone, octocrylene, and octinoxate sunscreen ingredients on cucumber plants (*Cucumis sativus* L.). Sci Total Environ 714, 136879 DOI: 10.1016/j.scitotenv.2020.136879.

Hayden, C.H.J., Roberts, M.S., Benson, H.A., 1997. Skin absorption of oxybenzone in humans. Lancet 350l863-864 DOI: 10.1016/S0140-6736(05)62032-6.

Huo, W., Cai, P., Chen, M., Li, H., Tang, J., Xu, C., Zhu, D., Tang, W., Xia, Y., 2016. The relationship between prenatal exposure to BP-3 and Hirschsprung's disease. Chemosphere 144, 1091-1097 DOI: 10.1016/j.chemosphere.2015.09.019.

Gonzalez, H., Farbrot, A., Larko, O., Wennberg, A-M., 2005. Percutaneous absorption of the sunscreen benzophenone-3 after repeated whole-body applications, with and without ultraviolet irradiation. British J Dermatol 154, 337-340 DOI: 10.1111/j.1365-2133.2005.07007.x.

Janjua, N.R., Kongshoj, B., Andersson, A-M., Wulf, H.C., 2008. Sunscreens in human plasma and urine after repeated whole-body topical application. J Euro Acad Dermatol Venerol 22, 456-461 DOI: 10.1111/j.1468-3083.2007.02492.x

Khalid, M. Abdollahi, M., 2021. Environmental distribution of personal care products and their effects on human health. Iranian J Pharmaceut Res 20, 216-253 DOI: 10.22037/IJPR.2021.114891.15088.

1023 Matta, K.M., Zusterezell, R., Nageswara, R.P., Vikram, P., Volpe, A.V., Florian, J., et al., 2019.
1024 Effect of sunscreen application under maximal use conditions on plasma concentration of
1025 sunscreen active ingredients: a randomized clinical trial. JAMA 321, 2082-2091 DOI:
1026 10.1001/jama.2019.5586.
1027
1028 Matta, M.K., Florian, J., Zusterzeel R., Nageswara, R.O., Patel, V., Volpe, D.A., 2020. Effect of
1029 sunscreen application on plasma concentration of sunscreen active ingredients: a randomized
1030 clinical trial. JAMA 323,256-267 DOI: 10.1001/jama.2019.20747.
1031
1032 Sarveiya, V., Risk, S., Benson, H.A.E., 2004. Liquid chromatographic assay for common
1033 sunscreen agents: application to in vivo assessment of skin penetration and systemic absorption
1034 in human volunteers. J Chromatography B 803, 225-231 DOI: 10.1016/j.jchromb.2003.12.022.
1035
1036 Wang, J., Meng, X., Feng, C., Xiao, J., Zhao, X., Xiong, B., Feng, J., 2021. Benzophenone-3
1037 induced abnormal development of enteric nervous system in zebrafish through MAPK/ERK
1038 signaling pathway. Chemosphere 280, 130670 DOI: 10.1016/j.chemosphere.2021.130670.
1039
1040 Wnuk, A., Rzemieniec, J., Staron, J., Litwa, J., Lason, W., Bojarski, A., Kajta, M. 2018. Prenatal
1041 exposure to benzophenone-3 impairs autophagy, disrupts RXRs/PPAR signaliing, and alters
1042 epigenetic and post-translational statueses in brain neurons. Molecular Neurobiol 56, 4820-4837
1043 DOI: 10.1007/s12035-018-1401-5.
1044
1045 Wnuk, A., Rzemieniec, J., Litwa, E., Wladyslaw, L., Kajta, M., 2018. Prenatal exposure to
1046 benzophenone-3 (BP-3) induces apoptosis, disrupts estrogen receptor expression and alters the

epigenetic status of mouse neurons. J Steroid Biochem Molecul Biol 182,106-118 DOI:
10.1016/j.jsbmb.2018.04.016.

Figure and Table Legends

Figure 1. *Panel A* - Sampling locations and oxybenzone concentration within Hanauma Bay, Oahu, State of Hawaii, U.S.A. Water samples were collected approximately 30 cm below the water surface. *Panel B* - Beach sand sampling locations within the run-off plume of the two beach showers in Hanauma Bay, City of Honolulu, State of Hawaii, U.S.A. Sand samples (indicated by numbers in red squares) consisted of collecting the top 5 cm of surface sand within a ~10 cm x 10 cm sampling square and were collected on January 27, 2020. Numbers designating sample sites are the same designations in **Table 1**. Arrows indicate observable rivulets from shower run-off.

Figure 2. Model results for Scenario #1 (assuming the presence of pure tidal currents) – the concentration releases at a unit rate at five locations inside the bay during the period of 9 am to 4 pm on November 10th, 2018, and the concentration distribution is shown after (A) 3 h, (B) 9 h, (C)15 h, (D) 21 h, (E) 27 h, (F) 33 h, (G) 39 h, (H) 45 h, (I) 51 h, (J) 57 h and (K) 63 h. The retention time is the longest under these conditions.

Figure 3. Model results for Scenario #2 (in the presence of southward oceanic currents) – the concentration releases at a unit rate at five locations inside the bay during the period of 9 am to 4 pm on November 5th, 2018, and the concentration distribution is shown after (A) 3 h, (B) 9 h and (C) 14 h. Most of the contamination is gone in less than a day.

Figure 4. Model results for Scenario #3 (in the presence of northward oceanic currents) – the concentration releases at a unit rate at five locations inside the bay during the period of 9 am to 4 pm on November 7th, 2018, and the concentration distribution is shown after (A) 3 h, (B) 9 h, (C) 15 h, (D) 21 h, (E) 27 h, (F) 33 h, (G) 39 h, and (H) 41 h. The retention time is much longer under these conditions.

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1077

1078 **Table 1**. Concentration of UV filters in sand samples expressed in micrograms of UV filter per
1079 gram of sand. BS = butyloctyl salicylate < LOQ = Below limit of quantitation, but detectable.
1080 <LOD = Below limit of detection.

1081

1082 **Table 2.** Hazard quotient for Acute Toxicity in Hanauma Bay, Oahu, Hawaii using US EPA
1083 method. Color chart: Red = Severe condition for a potential toxic effect, ≥ 0.5; Yellow –
1084 Moderate threat condition for a potential toxic effect, 0.1-0.5; Green = Low risk of acute toxicity,
1085 0.05- 0; Gold = ≥ 0.05 Acute Risk for endangered animal species

1086

1087 **Table 3.** Risk Quotient for Acute Toxicity in Hanauma Bay, Oahu Hawaii using European Union
1088 method for Cnidarian species, invertebrate (non-Cnidarian) species, plant and algae species, and
1089 fish species. Color chart: RED= Severe condition for a potential toxic effect ≥1; Yellow=
1090 Moderate threat condition for a potential toxic effect = 0.5 to 1.0; Green= Condition of concern
1091 0.5 to 0.1.

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Supplemental Table 1. Name, acronym and CAS Number of the organic UV filters and UV stabilizers investigated in the water extracts. Internal standards used for quantification were also included.

Supplemental Table 2. Performance of the HPLC-(ESI+)-MS/MS method applied.

Supplemental Table 3. Instrumental limit of detection in solution; limits of quantitation in solution and in sand samples. BS = butyloctyl salicylate. LOD = Limit of detection. LOQ = Limit of quantitation.

Supplemental Figure 1. The unstructured computational grid developed for the dispersion model.