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Toxicity and Hazards of Biodegradable and Non-Biodegradable Sunscreens to Aquatic Life of Quintana Roo, Mexico

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Abstract: Sunscreens have spread widely into aquatic systems over the last 18 years in Quintana Roo, Mexico. This contamination is caused by intensive use as a result of leisure activities, as sunbathers apply the substances intensively (up to 83.75% of tourists and locals). Moreover, 25% of the compounds are mainly released into the water through topical products washing off. On average, 300,000 tourists arrive every week in Quintana Roo, increasing the contamination. In addition, there are no recent studies on sunscreen toxicity and the hazards this represents for the native zooplankton of Quintana Roo. In order to assess their adverse effects, acute toxicity was assessed for nine sunscreens (five non-biodegradable and four biodegradable) in four zooplankton species (*Brachionus cf ibericus*, *Cypridopsis vidua*, *Diaphanocypris meridana*, and *Macrothrix triserialis*). In total, 21 LC₅₀ values were obtained, which are the baseline values for estimating risk and for determining the expected maximum permissible concentration. Our data on toxicity to freshwater species compared to marine species indicate that freshwater species are more sensitive than marine species. In conclusion, biodegradable sunscreen posed a moderate risk, and non-biodegradable posed a high risk. Our outcomes suggested that the maximum permissible concentrations for the contamination of sunscreens were 8.00E-05 g/L for non-biodegradable and 1.60E-04 g/L for biodegradable sunscreens.

Keywords: touristic impact; bioindicators; organic contamination; groundwater; Caribbean Sea

1. Introduction

The contamination of water caused by the intensive use of sunscreens is an environmental hazard. The tourism activity in coastal areas directly represents a major source of the contamination of marine and freshwater environments, because sunscreens contain organic and inorganic compounds that have adverse effects on the aquatic life [1]. These ingredients mostly reach the aquatic systems through the washing off of topical products used by tourists and the local population, which eventually contaminate the marine environments, freshwater systems (dolines and karstic lakes) and wildlife [2,3]. The contamination of ecosystems by sunscreens is directly related to anthropogenic activities, mainly in coastal tourist destinations. The discharge of sunscreens in tourist destinations is high, and in coastal tourist destinations with aquatic activities taking place in direct sunlight, sunscreen use increases and the problem is magnified [4]. Direct discharge is significant in quantitative terms, most probably due

to the contamination of water by sunscreens. For example, in seawater, the minimum concentration detected is $3.03\text{E-}13$ g/L, and the maximum is $1.00\text{E-}09$; in wastewater treatment plants (WWTP), the minimum is $5.49\text{E-}13$, and the maximum is $1.00\text{E-}07$; and, in general, for surface water, the minimum is $2.28\text{E-}13$, and the maximum is $1.00\text{E-}07$ [4,5]. Approximately 25% of the sunscreen applied on the skin washes off in direct contact with water [6]. In the particular case of coastal tourist destinations, Casas-Beltran et al. [7] estimated that more than 4000 tons of sunscreens have been added in the last 20 years by tourists and locals into the aquatic ecosystems of the Mexican Caribbean. Within the commercial range of sunscreens used by tourists and locals, there are conventional options (made with substances derived from oil and considered non-biodegradable), while other options are considered “friendly” to the environment, such as biodegradable sunscreen, classified by manufacturers as containing natural ingredients or products that they consider to be less harmful to the environment and aquatic life (Federal Office of the Consumer (PROFECO in Spanish)).

The number of tourists that visit the Mexican Caribbean is immense and, as a consequence, the discharge of sunscreen is increasing. This presents an adverse scenario for the ecosystem, aquatic life and human health. It is estimated that there are 1.2 million tourists on average per month in Quintana Roo, which indicates that sunscreen discharge is continuous and the ingredients in sunscreens could intensify their presence and concentration in the water and biota. In the Mexican Caribbean, water pollution is a serious problem for wildlife and the tourism economy. This is especially true for Quintana Roo, Mexico, in which tourism is an important sector of economic development; in fact, this zone receives 87% of the total tourist flow that arrives in the state [8]. The use of sunscreens by the millions of tourists who arrive every year increases the contamination of sunscreens in aquatic systems, mainly because it is considered that 89.9% of the tourists carry out aquatic activities [7]. According to Rodríguez-Fuentes et al. [9], 83.75% of sunbathers use sunscreen in Quintana Roo. The ingredients of sunscreens could contain pollutants. The concerns intensify for society, public health and the tourism sector, because the wastewater treatment coverage in the state is low; only 68% of wastewater is treated. This results in the immense contamination of toxic compounds in aquatic systems, which are potential stressing agents for the aquatic biota of the state of Quintana Roo.

It is estimated that more than a thousand tons of sunscreen are discharged each year in aquatic systems, with more than 50 different ingredients being discharged. The presence of dozens of chemical compounds in the water increases toxicological interaction and the adverse effects are complex. It is essential to mention that all sunscreens contain several highly toxic ingredients; unfortunately, their adverse effects are devastating, inducing moderate to high mortality according to scientific reports. The behavior of the components of various sunscreens depends on their molecular characteristics, and the presence of certain functional groups are factors that determine their toxicity. Their adverse effects on the biota can cause endocrine disruption, bioaccumulation or biomagnification [2,3,10–12]. The majority of the compounds are not soluble in water, and degrade by photolysis. Their half-life is less than 20 days. The ingredients of sunscreens that are discharged in the aquatic systems are diluted; therefore, the biological effects on aquatic life depend on the magnitude of sunscreens introduced into the ecosystem. Consequently, the places with a greater prevalence of aquatic activities will be the most frequently contaminated.

In addition, little work has been done in ecotoxicology for these sites; in fact, there are no current data on the toxicity of sunscreens on native species, nor any risk assessment for Quintana Roo, Mexico. As a starting point, in the present study, our hypothesis is that biodegradable sunscreens are less toxic than non-biodegradable ones to native zooplankton. Additionally, toxicity data provide a baseline for carrying out contamination risk assessments and performing toxicological tests to determine the toxicity caused by sunscreens in aquatic ecosystems. With our current knowledge, we suggest reference values for future aquatic toxicology research. The goal was to calculate the reference values of sunscreens (in g/L), as a guide for decision-makers in the development of ecotouristic parks and for environmental protection agencies. The worst risk scenario in Quintana Roo is that sunscreen ingredients probably transfer from one aquatic system to another. Assessing this adverse scenario

should take priority, due to the connectivity and the groundwater flows of the karstic systems of Quintana Roo.

2. Materials and Methods

2.1. Zooplankton Sampling and Identification

Zooplankton was collected in two aquatic systems in Quintana Roo. We completed limnetic and littoral drag sampling using a Wisconsin zooplankton net of 54 μm mesh aperture, filtering approximately 500 mL of water per drag. Half of the sample (250 mL) was preserved with 4% formalin for taxonomical identification and the other 250 mL was kept at room temperature to perform the isolation of organisms in the laboratory and then culture them (Ecotoxicology Laboratory of the Water Sciences Unit, Yucatan Centre for Scientific Research CICY). To identify the zooplankton species, we used the dichotomy and pictorial keys of Mills et al. [13] Elías et al. [14] for cladoceran, and Nagler et al. [15] for ostracods. Samples were identified with an inverted Nikon Eclipse microscope (Tokyo, Japan), model TS 100, and with a stereoscopic Nikon SMZ745 microscope, model C-LEDS.

2.2. Isolation and Creation of Monoclonal Cultures of the Zooplankton Species

For the creation of monoclonal cultures of zooplankton, we followed the standardized protocols of Lopez-Gutiérrez et al. [16], Pérez-Legaspi et al. [17] and Garza-León et al. [18]. Two monoclonal cultures of rotifers were established: Sian Ka'an (19.088533N, -87.550750W) and Cancun (21.199675N, -86.818698W), with two different monoclonal cultures for ostracods (21.202753N, -86.840897W) and one for cladocerans (21.182637N, -89.813456). Rotifers and the cladocerans *Macrothrix tricerialis* were fed the microalgae *Nannochloropsis oculata*. The ostracods *Cypridopsis vidua* and *Diaphanocypris meridana* were fed common commercial lettuce and the microalgae *N. oculata*. The organisms were placed in Petri dishes with EPA (US Environmental Protection Agency) medium [19] containing 96 mg/L of NaHCO_3 , 60 mg/L of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 60 mg/L of $\text{SO}_4 \cdot 7\text{H}_2\text{O}$, and 4 mg/L of KCl, pH of 7.5, with a hardness of 80–100 and an alkalinity of 57–64, expressed as mg CaCO_3/L . The green algae *N. oculata* Droop, 1955 (LB164 strain from the University of Texas collection) was cultivated in Bold's media [20]. All organisms were cultivated in a bioclimatic chamber with a photoperiod of 16:8 h (light/dark), at a temperature of 25 ± 2 °C. The processes of acclimatization took at least 2 months.

2.3. Sunscreen Selection and Preparation of the Sunscreen Stock

Sunscreens were selected from the data reported by the Federal Consumer Office, Mexico (PROFECO), as reported by Rodríguez-Fuentes et al. [9], and according to a prospective study carried out at the public entrances of two tourist beaches in the city of Cancun (Playa Delfines and Playa Gaviota Azul), and one cenote with touristic activity (Cenote Verde Lucero, Puerto Morelos), based on the methodology and sampling sites from Casas-Beltrán et al. [21]. The survey consisted of structured questions and was codified for further statistical analysis (see the Supplementary Materials). Prospective surveys were carried out from January to March 2018. The target group included tourists older than 18 years, who had spent at least one night in the location where they were sampled. Sampling was systematically taken at visitor exit points, reaching a sample size of 208 persons.

For the toxicity experiments, five commercial brands of non-biodegradable sunscreen and four biodegradable sunscreens were chosen; these were given codes—the information is shown in Table 1. The sunscreen solutions were prepared as follows: 1 g of sunscreen was placed in a 100 mL Erlenmeyer flask, and then we added 100 mL of the culture media (either freshwater or saltwater).

Depending on the species, the samples were cultivated in freshwater or saltwater. The flasks were placed in an orbital Shaker CVP-100B incubator, for 2 h at 200 rpm and 25 °C. We used ten nominal concentrations: 1.00E-02, 2.50E-02, 5.00E-02, 1.00E-01, 2.50E-01, 1.0E+00, 2.5E+00, 5.0E+00 and 1.00E+01 g/L. Before the final exposure concentrations, exploratory tests were carried out to obtain the final exposure range.

2.4. Acute Toxicity Test in Zooplankton

The experimental methods were designed following the Environmental Protection Agency manual, “Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms” [19], Pérez-Legaspi and Rico-Martínez [22], Santos-Medrano et al. [23], and López-Gutiérrez et al. [16], and adapted to the organism used in each test. For rotifers, sterile 24-well Costar® polystyrene plates were used. Ten newborns per species were placed in 1 mL of culture media. Each well had a repetition and an exposure replica. Each repetition and replica had a control without sunscreen added (reference blank). Mortality was recorded at 24 h in order to obtain the LC₅₀ values (the concentrations of the sunscreen in water in g/L that killed 50% of the test animals during the observation period). For ostracods and cladocerans, sterile 24-well Costar® polystyrene plates were used. Ten newborn ostracods and five newborn cladocerans were placed in 1 mL of freshwater media with their respective sunscreen concentrations; 10% mortality was accepted in the control groups. In total (without taking into account the prospective experiments of acute toxicity), we used 12,960 rotifers (3240 organisms for each strain; Sian Ka’an and Cancun), 6480 ostracods (3240 for each species) and 720 cladocerans. The Maximum Allowable Toxicant Concentration (MATC) was calculated with the geometric mean of LC₁₀. In addition, the LC₅₀ and LC₁₀ values were calculated by means of a linear regression analysis and Probit model, using Statistica® Version 6 (StatSoft Inc. Tulsa, OK, USA).

2.5. Risk Assessment and Statistical Analyses

Risk assessments were carried out for the five non-biodegradable and four biodegradable sunscreens on the five aquatic species previously mentioned. From the LC₁₀ values, we obtained the MATC, and then estimated the maximum permissible concentration for the predicted no effect concentration (PNEC). PNEC were used to estimate environmental risk assessments, according to Karlsson [24], Zhao and Chen [25], Cruzero et al. [26], and Wijngaarden et al. [27], by commonly using one species from every trophic level—microalgae, cladocerans and fish. However, several authors used one or two species, notably by applying an appropriate assessment factor (AF = 1000) to compensate for the intra- and inter-laboratory variation, biological variance, and extrapolation from the lab to the field [28].

A risk assessment (RQ) was carried out using the following formula:

$$\begin{aligned} RQ &= \frac{MEC}{PNEC} \\ PNEC &= \frac{MATC}{AF} \end{aligned} \quad (1)$$

where MEC is the environmental concentration of the pollutant, PNEC is the predictive concentration at which no adverse effect is observed, MATC is the maximum allowable toxicant concentration and AF is the assessment factor. The interpretation of RQ values was as follows: <0.1 = negligible risk; 0.1–1.0 = low risk; 1.0–10 = moderate risk; and >10 = high risk. As a reference for interpretation, a low PNEC value meant the toxicity of the substance was high, while a high value of PNEC meant that the toxicity of the substance was low. In risk assessments, PNEC must always be high with regard to the environmental concentration of the substance in question; on the contrary, environmental risk increases according to the interpretation of Beyer et al. [28]. As a second step in the assessment of environmental risks, the environmental concentration of the pollutant (MEC) was obtained from the information taken from the scientific literature on the environmental concentrations of the components of the sunscreens used in these toxicity tests.

3. Results

3.1. Statistics on Sunscreens, Quintana Roo, Mexico

The results obtained from the 208 surveys carried out in Quintana Roo identified 54 brands of sunscreens, of which 12.96% are classified as biodegradable and 87.03% as non-biodegradable.

The brands most used by the tourists in the three sites were Coopertone Babe[®], Hawaiian Tropic[®], Nivea Sun[®], and Banana Boat[®]. Sunscreens used in Quintana Roo that were cataloged as biodegradable were the following: Kiinsun, Maya Solar, Protectyl Vegetal, and Hawaiian Tropic[®].

The potential introduction of sunscreen via skin washes in tourists was high, since 67% of the tourists surveyed admitted to having used sunscreen and, of these, the average application was 2.16 times per hour. The sites that could have the greatest contribution of sunscreen per visit by tourists were beaches (47%), cenotes (22%), mangroves (12%) and thematic parks (19%), with the averages of the visits to each site being 2.3, 1.4, 1.1 and 1.2 respectively. On the other hand, despite this, there was generally some awareness among respondents about the impact of sunscreens in aquatic environments. A total of 67% of respondents recognized that sunscreens in some way or another produce an adverse effect on the biota of aquatic environments, although it should be noted that only 35% recognized that non-biodegradable sunscreens could also produce negative effects on the biota. Finally, despite this, 92% of the respondents would be willing to use other alternative methods of sun protection (Sun-Protective Clothing). For more details, see the conceptual contamination model of sunscreens in Figure 1.

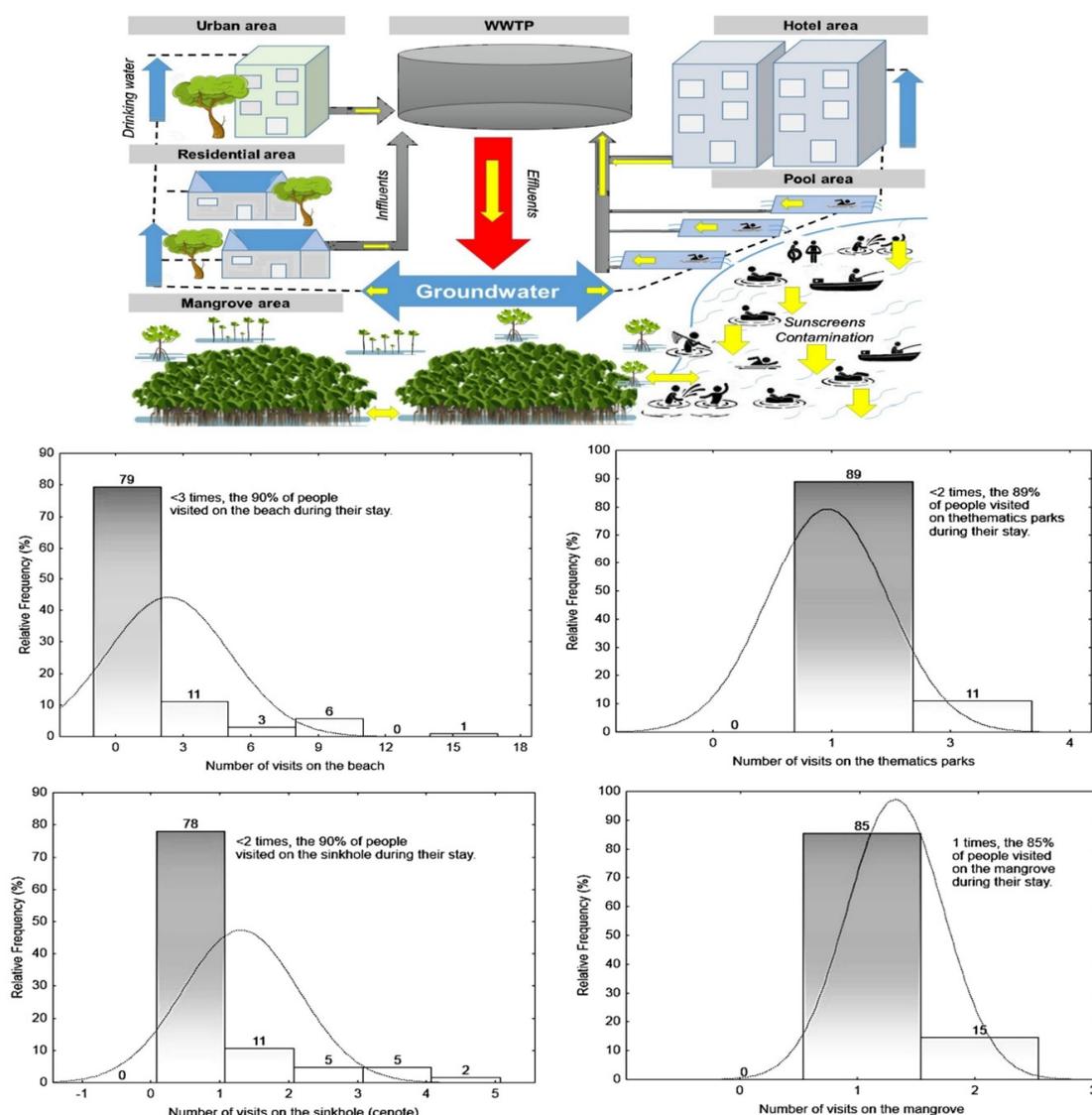


Figure 1. Fitting of continuous distributions (relative frequency %) from interviews of 208 people in three sites (two beaches and one sinkhole) in Quintana Roo. The yellow arrow in the conceptual contamination model indicates the direct discharge of sunscreen to water and its distribution from the aquatic systems to the aquifer, then from drinking water to the wastewater treatment plant (WWTP).

3.2. Bioindicator Species

Four species were isolated from two aquatic ecosystems in the state of Quintana Roo: *Brachionus* cf. *ibericus* (marine rotifer), *Macrothrix triserialis* (freshwater cladoceran), *Diaphanocypris meridana* (freshwater ostracod), and *Cypridopsis vidua* (freshwater ostracod). These species acclimated to laboratory conditions acceptably. All species were isolated from the coastal area of Quintana Roo, the cladocerans and the rotifers are eurihaline species, while the ostracods are freshwater. The four species (five monoclonal cultures) represent a group comprised of specific species that are useful for aquatic toxicology studies in the aquatic ecosystems of Quintana Roo.

3.3. Toxicity of Sunscreens in Zooplankton Species

A total of 21 values for LC₅₀ were obtained. All the LC₅₀ values are shown in Table 1. The most significant results from the toxicity tests of biodegradable sunscreens were found for Hawaiian Tropic™ Biodegradable (TBO, B4), which was the most toxic for zooplankton, with an LC₅₀ value of 1.80E-01 g/L. Sunscreen Kiin Sun (B-1) was the least toxic for zooplankton and its LC₅₀ value was 6.77E+00 g/L. Regarding non-biodegradable sunscreens, Banana Boat (NB1) was the most toxic, with an LC₅₀ value of 3.00E-02 g/L. Nivea Sun (NB-5) was the least toxic and its LC₅₀ value was 2.46E+00 g/L.

Table 1. Acute toxicity of biodegradable (B) and non-biodegradable (NB) sunscreens to native zooplankton of Quintana Roo, Mexico. Clone culture in laboratory conditions (C). BO = Biodegradable; ST= Sheer Touch; O = Ozone.

Species	Sunscreens	Keys	r ²	LC ₅₀ g/L	LC ₁₀ g/L
<i>Brachionus</i> cf. <i>ibericus</i> SianKan C7	Kinsun	B1	0.888	1.68E+00	7.00E-01
<i>Cypridopsis vidua</i>	Kinsun	B1	0.921	1.53E+00	4.51E-01
<i>Diaphanocypris meridana</i>	Kinsun	B1	0.999	6.77E+00	7.00E-01
<i>D. meridana</i>	Maya Solar	B2	0.978	3.90E-01	1.00E-02
<i>Cypridopsis vidua</i>	Protectyl Vegetal	B3	0.891	3.40E-01	8.00E-02
<i>Brachionus</i> cf. <i>ibericus</i> Cancun C16	Hawaiian Tropic™ BO	B4	0.932	5.00E-01	1.60E-01
<i>B. cf ibericus</i> Cancun C20	Hawaiian Tropic™ BO	B4	0.736	6.50E-01	1.90E-01
<i>B. cf ibericus</i> SianKan C6	Hawaiian Tropic™ BO	B4	0.898	6.30E-01	2.20E-01
<i>B. cf ibericus</i> SianKan C7	Hawaiian Tropic™ BO	B4	0.907	5.40E-01	1.70E-01
<i>Cypridopsis vidua</i>	Hawaiian Tropic™ BO	B4	0.903	3.30E-01	1.80E-01
<i>Diaphanocypris meridana</i>	Hawaiian Tropic™ BO	B4	0.872	1.80E-01	4.00E-02
<i>Cypridopsis vidua</i>	Banana Boat	NB1	0.893	2.10E-01	1.00E-01
<i>Diaphanocypris meridana</i>	Banana Boat	NB1	0.824	1.00E-01	1.00E-02
<i>Macrothrix triserialis</i>	Banana Boat	NB1	0.917	1.00E+00	4.60E-01
<i>Cypridopsis vidua</i>	Coopertone Babe	NB2	0.839	2.30E-01	1.10E-01
<i>Diaphanocypris meridana</i>	Coopertone Babe	NB2	0.947	2.30E-01	7.00E-02
<i>D. meridana</i>	Hawaiian Tropic™ ST	NB3	0.869	1.80E-01	5.00E-02
<i>Macrothrix triserialis</i>	Hawaiian Tropic™ ST	NB3	0.804	2.70E-01	7.00E-02
<i>Cypridopsis vidua</i>	Hawaiian Tropic™ O	NB4	0.937	2.30E-01	4.00E-02
<i>Diaphanocypris meridana</i>	Hawaiian Tropic™ O	NB4	0.946	4.80E-01	2.00E-02
<i>D. meridana</i>	Nivea Sun	NB5	0.934	2.46E+00	6.60E-01

The Maximum Allowable Toxicant Concentration (MATC), obtained using our acute LC₁₀ values, is shown in Table 1. In general, the biodegradable sunscreens' MATC was 1.57E-01 g/L, while for non-biodegradable sunscreens, it was 7.60E-02 g/L. The MATC of Nivea Sun (NB5) was the highest, and its value was 6.60E-01 g/L, while Maya Solar was the lowest and its value was 1.00E-02 g/L. The calculated PNECs in g/L are shown in Table 2. PNEC can be used as the suggested maximum permissible concentration of contamination by sunscreens; according to our toxicity results, the suggested maximum permissible concentrations of contamination by sunscreens are, for non-biodegradable sunscreens, 8.00E-05 g/L and, for biodegradable sunscreens, 1.60E-04 g/L.

3.4. Risk Assessment

Based on the previous results, environmental risk assessments for the biodegradable and non-biodegradable sunscreens were carried out. For these analyses, LC₁₀ values were used, as well as the environmental concentration of components present in the sunscreens (MEC = 1.00E-03 g/L), according to Karlsson [24], Zhao and Chen [25], Cruzeiro et al. [26], and Wijngaarden et al. [27]. Based on our results, each sunscreen had a different risk characterization, based on the toxicity found in toxicological tests. The results of the risk assessment are shown in Table 2. The sunscreens with high risks to aquatic life were Maya Solar, Banana Boat, Coopertone®Babe, Hawaiian Tropic™ Sheer Touch and Hawaiian Tropic™ Ozone. Those with moderate risks to aquatic life were Kinsun, Protectyl Vegetal and Nivea Sun. In general, biodegradable (B) sunscreen posed moderate risks to aquatic life, while non-biodegradable (NB) posed high risks to aquatic life.

Table 2. Risk assessment and toxicity of sunscreens, according to LC₁₀ values estimated using zooplankton from Quintana Roo, Mexico. Maximum Allowable Toxicant Concentration (MATC). BO = Biodegradable; ST= Sheer Touch; O = Ozone.

Sunscreens	Keys	MATC of LC ₁₀ in g/L	PNEC in g/L	RQ = MEC (0.001 g/L)/PNEC	Interpretation
Kinsun	B1	6.05E-01	6.05E-04	1.65E+00	Moderate
Maya Solar	B2	1.00E-02	1.00E-05	1.00E+02	High
Hawaiian Tropic™ BO	B3	1.42E-01	1.42E-04	7.04E+00	Moderate
Protectyl Vegetal	B4	8.00E-02	8.00E-05	1.25E+01	High
Banana Boat	NB1	7.72E-02	7.72E-05	1.30E+01	High
Coopertone®Babe	NB2	8.77E-02	8.77E-05	1.14E+01	High
Hawaiian Tropic™ ST	NB3	5.92E-02	5.92E-05	1.69E+01	High
Hawaiian Tropic™ O	NB4	2.83E-02	2.83E-05	3.54E+01	High
Nivea Sun	NB5	6.60E-01	6.60E-04	1.52E+00	Moderate
Biodegradable	B	1.57E-01	1.57E-04	6.36E+00	Moderate
Non-Biodegradable	NB	7.61E-02	7.61E-05	1.31E+01	High

4. Discussion

The toxicity data hereby obtained is considered as a baseline for understanding the risks to aquatic life in Quintana Roo. Acute toxicity in zooplankton species was mainly obtained with original sunscreen formulations, which are actually a mixture of components, with a few recognized as active ingredients and the rest as part of the formulation. The sensitivity of the zooplankton species studied ranged between LC₅₀ values of 1.00E-01 g/L and 6.7E+00 g/L. It is important to stress that the evaluated toxicity refers to the mixture of components present in one single formula, and the adverse effects of a single chemical may not be captured, or it can be altered, owing to interactions between chemicals and the physiochemical properties of the substances in the solution [29,30]. Consequently, the toxicity of sunscreen was difficult to assess during the exposure tests, because the complexity of the sunscreens typically include a combination of oxybenzone, avobenzone, octisalate, octocrylene (OCT), homosalate and octinoxate, and other substances. Additionally, the water solubility of the ingredients is different. For example, according to PubChem [31], the solubility for camphor is 1.60E+00 g/L, for benzophenone it is 1.37E-01 g/L, for triazone it is 2.30E+02–3.50E+02 g/L, for drometrizole it is 7.03E-05 g/L, OCT is 6.85E-02 g/L, for titanium dioxide (TiO₂) it is <1.00E+00 g/L and, for zinc oxide (ZnO), it is 7.45E-03 g/L.

In other studies, the toxicity of isolated ingredients in indicator species has been determined. For example, reports on anatase and rutile acute toxicity in cladocerans and rotifers produced LC₅₀ values between 9.90E-04 g/L and 9.47E-02 g/L—a lower range than our results. In addition, when compared with toxicological data obtained for cladocerans on acute toxicity from active ingredients such as oxybenzone and camphor, the LC₅₀ values ranged from 1.90E-03 to 5.00E-02 g/L [32]. Acute toxicity (LC₅₀) values in other aquatic species (*Pimephales promelas*, *Danio rerio*, and *Oncorhynchus mykiss*) range from 2.80E-04 g/L to 1.25E-01 g/L according to Kapler et al. [33], Heinlaan et al. [34] and Fent et al. [35]. Therefore, our acute toxicity values are higher than those of isolated ingredients.

Nonetheless, our baseline values contribute to the knowledge about risk assessments to the aquatic life of Quintana Roo, Mexico.

Contamination by sunscreens is complex and difficult to study, and the interpreted quantifications reported by several authors mention that sunscreen ingredients are variable, as a consequence of their variable use among the population and the intensity of water activities. For example, Gago-Ferrero et al. [36] studied three ingredients of sunscreens in wastewater treatment plants. According to their conclusions, 4-methyl-benzilidene-camphor (4MBC), OCT, and 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC) are high toxicity ingredients. The high concentrations of these components could be explained according to Balmer et al. [32] in a study conducted in Switzerland, where they reported that, for 10,000 people per day, the wastewater influent contained 118 g of EHMC, 4.90E+01 g of 4MBC, 6.90E+01 g of benzophenone-3 (BP-3), and 2.80E+01 g of OC. Additionally, contamination by sunscreen in the environment is extraordinarily inconstant, because it depends on the intensity of anthropogenic activities and because sunscreen enters ecosystems via the washing off of topical products used by tourists and the local population.

Tons of sunscreen are discharged to aquatic ecosystems, especially in touristic areas. For example, the discharge of EHMC, OCT, 4MBC and nanoparticles of TiO₂ has been estimated to be between 1 ton and more than 1000 tons per year. In this context, the study carried out by Casas-Beltran et al. [7] estimated that 4367.25 tons were discharged in the Mexican Caribbean in the last 18 years. Consequently, aquatic ecosystems are frequently contaminated by sunscreens. Likewise, it is important to consider that most of the compounds are not soluble in water, they degrade by photolysis and their half-life is less than 20 days, but they can also bioaccumulate [4]. According to a study carried out by Sanchez-Quiles and Tovar-Sánchez [4], the direct discharge of sunscreens is quantitatively the most probable method of contamination. For example, in seawater, the minimum concentration detected was 3.03E-13 g/L, and the maximum was 1.00 E-09; in wastewater treatment plants, the minimum was 5.49E-13 and the maximum was 1.00E-07, and, in general, for surface water, the minimum was 2.28E-13, and the maximum was 1.00E-07. In conclusion, the quantification data in water do not exceed 1.00E-03 g/L in surface water. However, it is important to mention that the discharge of sunscreens is continuous in coastal tourist sites (such as Cancun, Acapulco, Puerto Vallarta, Mazatlán and Los Cabos). In fact, the most important coastal tourist site is Cancun Quintana Roo, which receives ~50% of international tourism. It is reported that, in the Mexican Caribbean, every week, there are approximately 354,000 tourists, and a total of 17,146,971 tourists arrived in Quintana Roo in 2019 [7]. This implies that there is permanent water contamination by sunscreens throughout the year and, unfortunately, there are no quantification data in the aquatic ecosystems of Quintana Roo.

Moreover, the water activities that take place in Quintana Roo are located in areas with high permeability and rock porosity [7,21]. In addition to the entrance of sunscreens from recreational activities such as swimming and washing in sinkholes, mangles and coastlines (through direct contamination), they also enter the aquatic ecosystems via WWTPs via indirect contamination [32]. The allowed amount of ingredients used in the formulation of sunscreens has been specified: BP-3 is allowed up to 14%, while values of 8%, 48% and 52% are allowed for 4MBC, TiO₂ and ZnO, respectively. In other words, the most toxic ingredients are less prevalent. However, a contaminant that is not very toxic but it is used in large quantities can be toxic in the long term. The magnitude of ingredients that contaminate the water from the use of sunscreens is large, and the quantity of substances they contain increases the contamination problematic. The salts TiO₂ and ZnO present a hazard to life, as mentioned by Sánchez-Quiles et al. [4]; the nanoparticles of TiO₂ and ZnO that are contained in sunscreens are capable of producing H₂O₂, causing oxidative stress in marine organisms.

Sunscreens are persistent contaminants; the real magnitude of the problem of contamination of sunscreen ingredients in water is difficult to ascertain and can only be estimated [7]. Consequently, we consider this situation to be a hazard to aquatic life, because sunscreens have lethal and sublethal effects, they can bioaccumulate and biomagnify, and, consequently, they may cause mortality, morphological alterations and endocrine disruption in aquatic life [2,3,5,12]. Aquatic toxicology

tests are used in environmental risk assessments when we have concerns about the chemicals products release into water, such as sunscreens. The objective is to provide a guide to the potential hazards. Our data on sunscreen toxicity in freshwater zooplankton species compared to marine species indicate that freshwater species are more sensitive than marine species. However, despite the differences in toxicity, it is important to use both bioindicators to estimate the environmental risk, given that tourism and aquatic activities are carried out in various aquatic ecosystems, such as coral reefs, beaches, coastal lagoons, karst lakes and dolines. In addition, by using just one indicator or generalizing with one species, we would be underestimating the adverse effects of sunscreens on our aquatic ecosystems. Another important aspect to highlight is the increase in population in coastal areas and the associated tourism, which directly or indirectly increases the discharge of sunscreen into the water. For this reason, it is essential to quantify, in salt and freshwater, the formulations or active ingredients of sunscreen in order to identify the magnitude of the contamination in quantitative terms, particularly when there is a large tourist influx.

Finally, our outcomes suggest that the maximum permissible concentration of contamination by non-biodegradable sunscreens is $8.00E-05$ g/L and, for biodegradable sunscreens, it is $1.60E-04$ g/L, according to our risk assessment. These values correspond to the calculated predicted no effect concentration (PNEC) as an environmental quality standard (EQS), expressed as the maximum permissible concentration, according to Cruzero et al. [26]. In fact, these values indicate a concentration in water that produces adverse effects, and our values should be used to avoid these risks. The maximum allowable values calculated by us are two to three orders of magnitude below the maximum concentration suggested in water by several authors [3,6,32–36]. However, risk studies reported that 4MBC posed a high risk to algae, while BP-3 and EHMC were more likely to pose a risk to fish. [37]. In summary, the toxicities and risk assessments reported in the present study offer a wide-ranging analysis of the sensitivity of aquatic life to acute exposure to biodegradable and non-biodegradable sunscreens for 24 h.

5. Conclusions

Biodegradable sunscreen poses a moderate risk, while non-biodegradable sunscreen poses a high risk to the aquatic life of Quintana Roo, Mexico. Non-biodegradable sunscreens are the most-used sunscreens in Quintana Roo, Mexico, by tourists; therefore, the hazard is high and imminent for aquatic life according to our data. The discharge of sunscreens increases with the arrival of tourists to the coastal zone and touristic parks. The private sector, civil organization and environmental protection agencies of Mexico have attempted to increase the responsiveness among society and tourists to use non-toxic sunscreens or other sun protection methods. However, the influx increases every year; therefore, sunscreen studies must be multidisciplinary, require quantification studies of substances in water, and increase toxicity tests with native species to estimate the potential risks to the aquatic ecosystems that are the basis of the economy of Quintana Roo.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/12/8/3270/s1>, Figure 1. Fitting of continuous distributions (relative frequency %) from interviews of 208 people in three sites (two beaches and one sinkhole) in Quintana Roo, Table 1. Acute toxicity of biodegradable (B) and non-biodegradable (NB) sunscreens to native zooplankton of Quintana Roo, Mexico. Clone culture in laboratory conditions (C), Table 2. Risk assessment and toxicity of sunscreens, according to LC₁₀ values estimated using zooplankton from Quintana Roo, Mexico. Maximum Allowable Toxicant Concentration (MATC), and Survey.

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