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Abstract

Sunscreen provides protection against skin cancer by reducing UV exposure to the skin. Active ingredients come in two basic forms, chemical and mineral; ongoing research indicates that some active ingredients in sunscreen are harmful to marine life. This study is an analysis of chemical and mineral SPF 30 sunscreens to determine which provides the highest efficacy for skin protection while also providing the lowest toxicity to aquatic organisms. Sunscreen efficacy was tested by exposing photoreactive chemical paper applied with chemical and mineral sunscreens to the sun. Results of the photo effect paper trial showed a wide variation in the efficacy of SPF 30 rated sunscreen, ANOVA p=2.3E-09. Aquatic algae and mosquito larvae were exposed to a series of 6 different test solutions of sunscreens and a control over a 72 hour period. Results of showed statistically different effects of the 6 test solutions, with ANOVA p=0.0358 for mosquito survival and ANOVA p=6.27E-07 for the algae test. This study has demonstrated that brand reported sun protection factor is not accurate or consistent for all sunscreens tested. The results support other published research that indicates that the active ingredients in sunscreen can potentially cause significant harm to organisms in the environment.

Introduction

Worldwide there is a well-documented connection between sun exposure and risk of skin cancer. Yet, even with this well-established knowledge, the number of cases of skin cancer is still on the rise, now the most common form of cancer. Skin cancer can be broken down into two forms, melanoma, the more lethal form of skin cancer, and nonmelanoma, which can be further broken down into two common forms: Basal cell carcinoma (BCC) and Squamous cell carcinoma (SCC) (Skin Cancer Foundation, 2018). Research indicates that the pattern of sun exposure is a major factor in determining which type is presented. Melanoma is believed to be the result of brief, intense sun exposure such as a blistering sunburn, while non-melanoma is believed to be the result of accumulated sun exposure over several years of exposure as in regularly using a tanning bed (Huber, 2007). Data from the Connecticut Tumor Registry shows a significant increase in the number of incidences of melanoma cases from 1950-2007 with a 17-fold increase in men from 1.9 to 33.5 per 100,000 and a 9-fold increase in women from 2.6 to 25.3 per 100,000 (Geller et al., 2013). Additionally, the Centers for Disease Control and Prevention (CDC) states that from 1999 to 2015 the number of melanoma cases per year rose 200% from 40,000 to 80,000 and the death rates averaged 8,000 annually (CDC, 2018).

Sunscreen is the solution most heavily relied upon to combat the negative effects of the sun that lead to these skin cancers. There are many different companies manufacturing sunscreen, however all are creating sunscreen with the same handful of active ingredients. Sunscreen provides protection by reducing UV exposure to the skin through active ingredients that come in two basic forms: chemical and mineral. Chemical sunscreens include the active ingredients: oxybenzone, octocrylene, octisalate, homosalate, and avobenzone which provide protection after the solution is absorbed into the skin. Mineral sunscreens include the active ingredients zinc oxide (ZnO) and titanium dioxide (TiO_2) that provide protection as they stay on top of the skin (EWG, 2018). Whether companies use chemical or mineral ingredients, they are creating sunscreen concoctions by using their solutions of these active ingredients within other inactive base solutions. Meanwhile, many of these products do not work as advertised, a study of 650 different sunscreen products has shown that as many as 2/3 of products were either "harmful or ineffective".

While sunscreen is a popular way to protect oneself from sun exposure, there is evidence that indicates that the active ingredients can be harmful to human and animal health. Oxybenzone can result in organ system toxicity due to its absorptive property and accumulation in the bloodstream, liver and kidneys (Fediuk et al., 2011). Research on homosalate and other chemical UV-filters, found that they have the potential to cause hormone disruption (Krause et al., 2012). Oxybenzone has also been found to be harmful to corals by lowering the temperature at which corals will bleach. Oxybenzone can also damage coral DNA leading to lethal deformities, it is an endocrine disruptor leading to gender shifts in fish and has been found toxic to algae as well (Downs et al., 2015). Mineral sunscreens containing nanoparticles of zinc oxide and titanium dioxide have been found to react with UV light in water and create hydrogen peroxide which can impede phytoplankton growth (Sánchez-Quiles et al., 2014). In this case, the active ingredients may provide sun protection for human skin, but at the cost of significant harm. Oxybenzone related environmental problems can occur at levels as low as 62 parts per trillion. In comparison, levels measured in the water at Hawaiian beaches in the morning were higher than 700 parts per trillion and concentrations on other nearshore reefs are commonly measured between 100 parts per trillion and 100 parts per billion (Downs et al., 2015). These ranges significantly exceed the levels needed to classify sunscreen as an environmental threat, showing the alarming magnitude of the problem.

This study is an analysis of chemical and mineral sunscreens to determine which provides the highest efficacy for skin protection by blocking the sun's harmful rays while also providing the lowest toxicity to organisms. An experiment tested the efficacy of the sunscreen main active ingredients combinations: oxybenzone, octocrylene, octisalate, homosalate, avobenzone, titanium dioxide (TiO_2) and zinc oxide (ZnO) in protecting against sun exposure on a photoreactive substrate and were balanced against the effect of these same products on two groups of aquatic test invertebrate organisms: mosquito larvae and aquatic algae.

Hypothesis

H_A: Mineral based and chemical sunscreens will vary in their efficacy at reducing sun exposure.

H_0: Mineral based and chemical sunscreens will not vary in their efficacy at reducing sun exposure.

H_B: Mineral based and chemical sunscreens will vary in their toxicity to mosquitos.

H_0: Mineral based and chemical sunscreens will not vary in their toxicity to mosquitos.

H_C: Mineral based and chemical sunscreens will vary in their toxicity to algae.

H_0: Mineral based and chemical sunscreens will not vary in their toxicity to algae.

The independent variable for all the experiments was the active ingredients of the sunscreens. There were three chemical sunscreens used, one that had 5 active ingredients including avobenzone, homosalate, octisalate, octocrylene, and oxybenzone, one that had 4 active ingredients including avobenzone, homosalate, octisalate, and octocrylene, and one that had 3 active ingredients including avobenzone, homosalate, and octocrylene. Two mineral sunscreens were used, one included both non-nano titanium dioxide (TiO_2) and non-nano zinc oxide (ZnO) and one had only non-nano zinc oxide (ZnO). The dependent variables for the sun exposure experiment was the mean exposure of the photoeffect paper, for the aquatic organism experiments was the percent survival of the mosquitos and the scale of algal aggregation. The constants for all the experiments were the sunscreen brands with active ingredients used and the SPF of all of the sunscreens was 30. The constant in the exposure of the photo effect paper was time exposed. The constants in the mosquito and algae experiments were the sunscreen solutions and time exposed.

Materials and Methods

Efficacy of the sunscreen in blocking the sun's rays was tested using Nature Print Paper's photo effect paper. When exposed to the sun's rays, this white photoreactive chemical paper turns blue. Therefore, if the sunscreen is providing protection by blocking the incoming solar radiation, the paper will not be exposed and remain white. The experiment began by painting 2x2 cm squares of each SPF 30 sunscreen on the photo effect paper and then exposing it to the sun for 3 minutes. Following the instructions for the paper exposure, the sheet of paper was then submerged in water for 1 minute and then laid to dry. Any excess sunscreen that remained on top of the paper was removed, to reveal the exposure result. This trial was ran 8 times with 8 different SPF 30 sunscreen brands and the control, which was no product. A scale of 0-3 was used to quantify the level of protection from sun exposure of the paper after sunscreen treatment: 0 = no protection (dark blue color, full exposure of the paper), 1= minimal protection (medium blue), 2= moderate protection (light blue), and 3= good protection (white, no exposure of the paper).

To determine the effect of the sunscreen on aquatic organisms, an experiment with six different test solutions of sunscreen was created. The five test solutions were based on the active ingredient chemicals in the sunscreen brands, the absorption vs. spreading modes of chemical vs. mineral types of product. There were three treatments of absorbed sunscreens with three active ingredients, four active ingredients, and five active ingredients respectively. The three active ingredient sunscreen had avobenzone, homosalate, and octocrylene, the four active ingredient had avobenzone, homosalate, octisalate, octocrylene, and the five active ingredient had avobenzone, homosalate, octisalate, octocrylene, and oxybenzone. Also two treatments with the surface spread, non-absorptive, mineral based sunscreens: a non-nano titanium dioxide (TiO_2) and non-nano zinc oxide (ZnO) combination, and one with only non-nano zinc oxide (ZnO). These were tested against a control which included no sunscreen. The test solutions were created, concentrations did not exceed LD30 (PubChem), by placing 75 milliliters of water into an Erlenmeyer flask, and adding 0.5 g of sunscreen that had been weighed on an electronic balance. The Erlenmeyer flask was capped and shaken vigorously to homogenize the solution, and then dispensed out with a pipette in 15 ml volumes into five separate test tubes. This procedure was repeated five times resulting in 5 test tubes with 15 ml solutions of each sunscreen. The control consisted of 10 test tubes with 15 ml of water with no added sunscreen. For each treatment, 3 mosquito larvae were placed in each test tube and left for a 72-hour period. The mosquito larvae were examined and counted after 72 hours to see how many survived. The mosquito trial was then repeated for two 72 hour trials.

Another set of trials to determine the effect on photosynthetic algae was conducted using the same set up as the mosquito trials substituting aquatic algae for mosquito larvae. At the end of the 72 hour incubation period, samples were photographed using a compound microscope and a proscope video image analysis system. A scale of 0-3 was used to quantify the level of aggregation of algae due to exposure to sunscreen versus the control: 0= no aggregation, 1=minimal aggregation, 2=moderate aggregation, and 3=substantial aggregation. Data were analyzed statistically using ANOVA tests.

Results

Results of the photo effect paper trial showed a wide variation in the efficacy of purportedly SPF 30 sunscreen. Four of the SPF 30 sunscreens were ineffective at reducing sun exposure with only minimal to moderate sun blocking. Three ZnO brands scored 0, 1 and 1.5 respectively. The sunscreen that had both TiO_2 and ZnO scored the highest coverage at 3. Three of the four chemical sunscreen brands scored above the moderate level of 2 with the 4 ingredient scoring only 1.125. These data were analyzed using ANOVA, p=2.3E-09, which shows there is a statistical difference between the sun blocking power of these brands. A statistical t-test matrix (Table 1) was analyzed comparing each treatment to the control and the performance of each absorbing chemical treatment to the surface-lying mineral based treatment.

T-test Matrix	3 ing	4 ing	5 ing	ZnO	TiO_2ZnO	Control
Control	**0.000177**	**0.025555**	**0.000181**	**9.58E-05**		
TiO_2ZnO	**0.020938**	**0.002183**	**0.047945**	**9.58E-05**		
ZnO	0.099749	0.414702	0.065044		**9.58E-05**	**9.58E-05**

Table 1. The t-test matrix analyzes all treatments to the control and the chemical based treatments to the mineral based treatments. Those in bold represent significance. This shows that all brands provide better protection than the control. TiO_2ZnO provide significantly better protection than all the chemical based absorbing products. The ZnO was not statistically significant against the chemical based sunscreens.

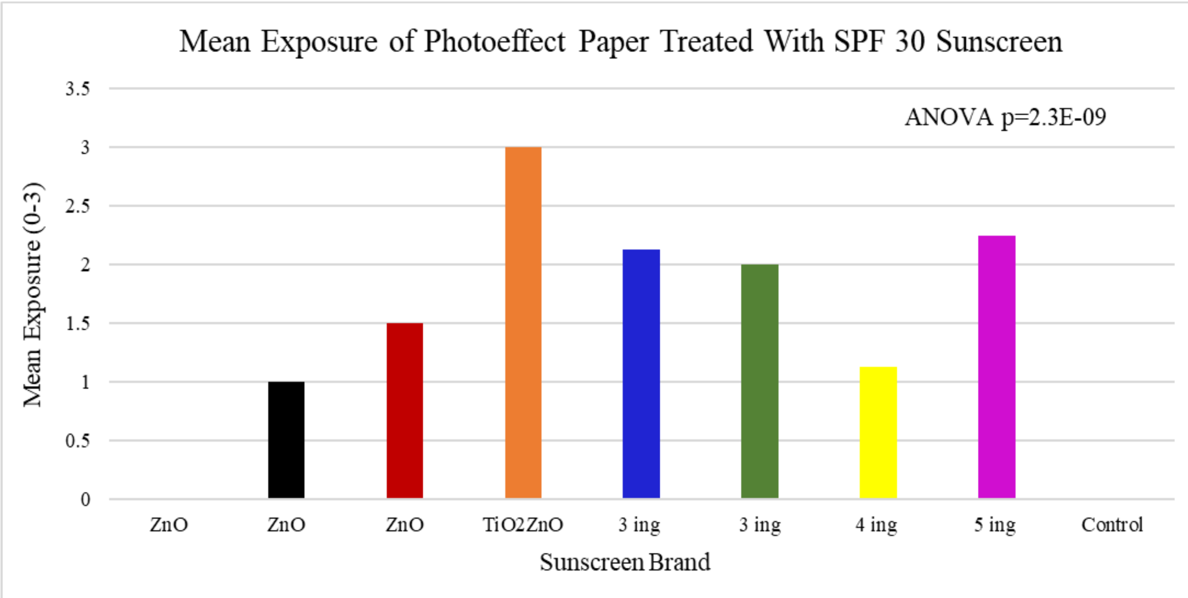

Figure 1. The mean exposure of the photoeffect paper is analyzed by brand on a scale of 0 least protection to 3 greatest protection, with widespread variation in 30 SPF sunscreen. TiO_2ZnO had the highest mean of 3, ZnO had means of 0, 1, and 1.5 respectively and the chemical based sunscreens ranged between 1.125 and 2.25. ANOVA p=2.3E-09 shows a statistical difference between the UV protection of these brands.

Results of the mosquito trials showed a range in toxicity of the sunscreen brands. The mineral based sunscreens, TiO_2ZnO and ZnO, and the control tested at the lowest toxicity levels with larval survival of 55%, 35%, and 40%, respectively. The chemical based sunscreens tested higher toxicity levels with the 3,4, and 5 ingredients sunscreens having percent survival rates of 20%, 20%, and 5%, respectively. The data were analyzed using ANOVA p=.0358, which shows

T-Test Matrix	3 ing	4 ing	5 ing	ZnO	TiO_2ZnO	Control
Control	0.170	0.238	**0.009**	0.295	0.730	
TiO_2ZnO	0.305	0.371	**0.036**	0.182		0.730
ZnO	**0.029**	**0.057**	**0.003**		0.182	0.295

Table 2. The percent survival of the mosquitos was significantly different in the 5 ingredient compared to the control, TiO_2ZnO, and ZnO. The ZnO was also significantly different against the TiO_2ZnO and the control. This data infers that the ZnO has the lowest toxicity to the mosquitos while the 5 ingredient has the greatest. The t-test matrix analyzes all treatments to the

control and the chemical based treatments to the mineral based treatments with those that are significant in bold.

there is a statistical difference between the toxicity of the sunscreen brands to the mosquitos. A statistical t-test matrix (Table 2) was analyzed comparing each treatment to the control and the toxicity of each chemical based treatment to the mineral based treatment.

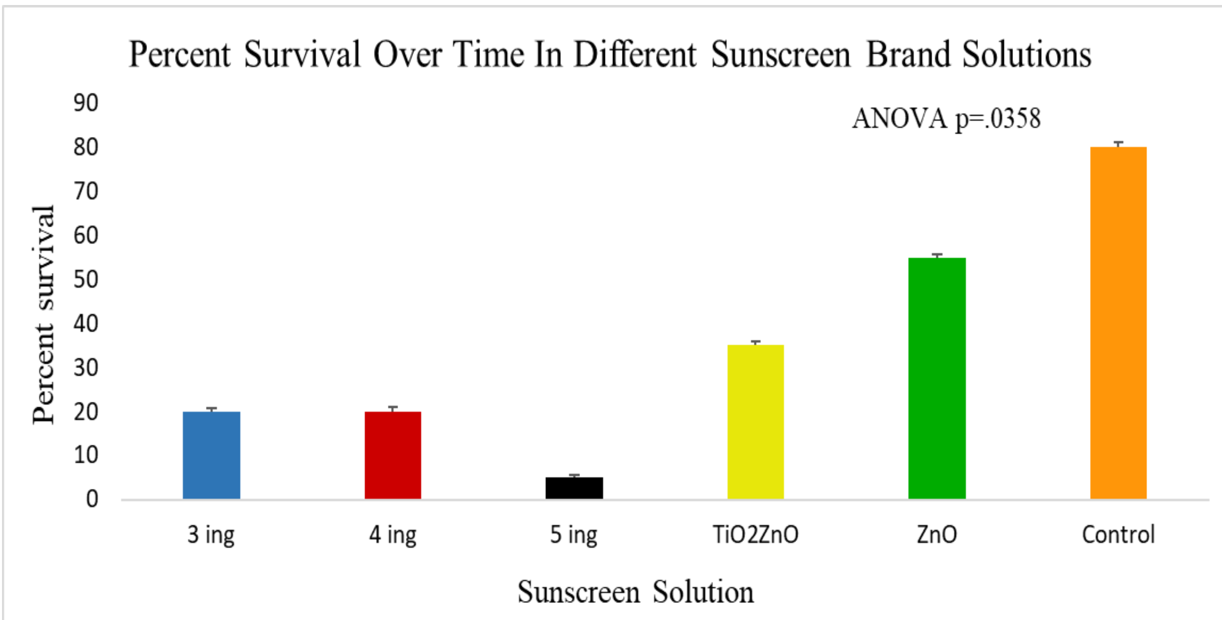

Figure 2. Mosquito larvae were exposed to sunscreen brands and had higher percent survival with ZnO, TiO_2ZnO, and the control having values of 55%, 35%, and 40%, respectively. The chemical based sunscreens had higher toxicity ranges with percent survival ranging from 5% to 20%. An ANOVA statistically analyzed the data with p=.0358 showing a statistical difference between the different sunscreen brands toxicity levels to the mosquito larvae.

Results of the algae trial showed a broad range in the degree of aggregation of the sunscreen brands. The control caused minimal aggregation with only a score of .2. The mineral based sunscreens had relatively low scores with the sunscreen with both TiO_2 and ZnO scoring 1.4 and the sunscreen with only ZnO scoring 1.6. The chemical based sunscreen brands caused substantial aggregation with the 3 ingredient, 4 ingredient, and 5 ingredient scoring 2, 3, and 3, respectively. The data was analyzed using ANOVA statistical analysis with p=6.27E-07 which shows a statistical difference between the aggregation levels of the sunscreen brands. Further analysis using a statistical t-test matrix (Table 3) compared each treatment to the control and the aggregation of each chemical based treatment to the mineral based treatment.

T-Test Matrix	3 ing	4 ing	5 ing	ZnO	TiO_2ZnO	Control
Control	**0.003**	**5.9E-09**	**5.9E-09**	**0.021**	**0.021**	
TiO_2ZnO	0.172	**0.003**	**0.003**	0.683		**0.021**
ZnO	0.455	**0.025**	**0.025**		0.683	**0.021**

Table 3. The t-test matrix analyzes all treatments to the control and the chemical based treatments to the mineral based treatments with those that are significant in bold. The control was significant against all treatments meaning that any exposure to chemical or mineral sunscreens has a significant impact on aggregation. The 4 ingredient and 5 ingredient held significance against both TiO_2ZnO and ZnO meaning that when algae is exposed to those chemical based sunscreens aggregation is significantly higher.

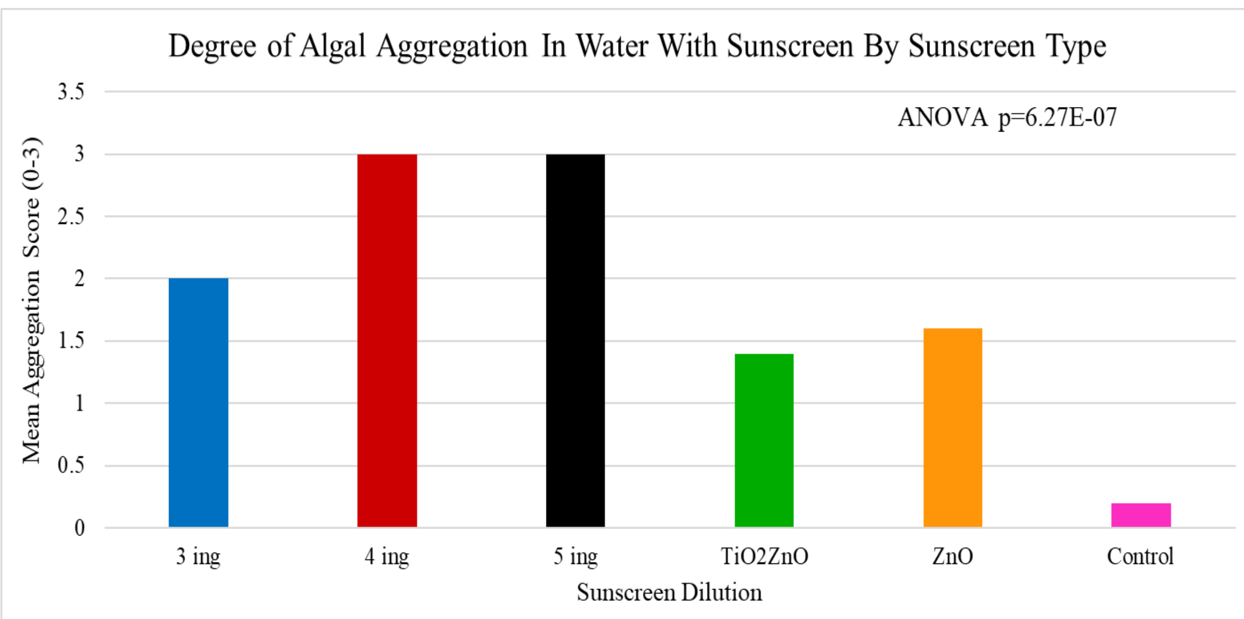

Figure 3. The aggregation levels of the algae when exposed to each sunscreen brand was analyzed on a scale of 0-no aggregation to 3-substantial aggregation depicting a wide range of results between the control, mineral based, and chemical based sunscreens. The control had the lowest aggregation with a mean value of .2. The mineral based sunscreens had slightly higher aggregation levels with ZnO scoring 1.6 and TiO_2ZnO scoring 1.4. The chemical based

sunscreens had substantial aggregation levels with the 3 ingredient scoring 2 and the 4 ingredient and 5 ingredient maxing out at a score of 3. An ANOVA statistically analyzed the data with p=6.27E-07 showing a statistical difference between the aggregation levels of the algae in the sunscreen treatments.

Conclusion

The photoeffect paper, mosquito trials, and algae trials all had a statistically significant p-value based off the ANOVA. The p-values of the photo effect paper, mosquito survival, and algal aggregation were p=2.3E-09, p=.0358, and p=6.27E-07, respectively. The significance of the three tests shows a statistical difference between mineral based and chemical based sunscreens and that the null hypotheses can be rejected for all three experiments.

This study shows that SPF, the sun protection factor, is not accurate. SPF is found through dividing the minimal time interval or UV dosage sufficient enough to produce perceptible erythema in non-sunscreen protected skin into the minimal time or UV dosage sufficient enough to produce perceptible erythema in sunscreen protected skin. (Dutra et al, 2004). Theoretically, all sunscreens with the same SPF should give the same protection, however this was disproven. All purportedly SPF 30 sunscreens did not provide the same UV protection meaning the sunscreen industry is falsely advertising and that new regulations need to be implemented along with new research for a method to achieve greater accuracy. The results also support new research on active ingredients in mineral based versus chemical based sunscreens. Research indicates the active ingredients in chemical based sunscreens can lead to significant harm in marine ecosystems including DNA damage in corals, acting as endocrine disruptors in fish, and toxicity to algae, while mineral based, non-nano titanium dioxide and non-nano zinc, are better alternatives. (Downs et al., 2015). Concluding statistical differences in the effects of the mineral versus chemical based brands supports this research and varying environmental effects.

The active ingredients in mineral based and chemical based sunscreens were tested for efficacy and environmental toxicity to see if there was a best solution. To better improve the findings of this study, more samples should be taken over a wider range of sunscreens. There are hundreds of different brands being used year-round each with their own make-up, so knowing what effects the ingredients have is an important start. Also, this study could be improved by including mineral sunscreens that use nanoparticles in the mineral based sunscreens to see the effect those implement vs the non-nano particles. Additionally, to better improve the findings of this study, advanced equipment and techniques need to be used to lessen error in the design and procedure. This study was attempted to get baseline knowledge of the concept and effects of sunscreen's active ingredients, but with more time and greater access to materials, a more in-depth understanding can be acquired.

One way this study could implement change is through consumer trends. Many buy sunscreens expecting protection and without concern of the effects. However, this study proves that not all sunscreens offer the same protection, and that's how attention could be gained. The attention could then be used to act for protection. This study can be applied to show proof that governmental action needs to take place. In coastal and tropical communities, sunscreen is applied year-round and in vast amounts. Showing that different active ingredients pose different threats, governmental action can be done to ban certain brands while still allowing others. For example, this has already taken place in Hawaii to try and protect their marine ecosystems. Additionally, this study opens doors for funding for more research. Proving that there is a statistical difference between brands can lead communities to want to know more on how to protect their fragile environments in which they depend upon. The understandings of this topic are still coming to light, but this study adds evidence that there are changes that need to be made and it can be a driving force for the action to happen.

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