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The Plastic Pandemic: Examining Surgical Face Mask Degradation in the Marine Environment in Times of COVID-19

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By

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Abstract:

The development and use of single-use plastics skyrocketed with the onset of the COVID-19 pandemic in 2020. With the support of world governments, manufacturing companies exponentially increased their output of personal protective equipment (PPE), and wearing surgical grade face masks became a ubiquitous aspect of reopening public society as they proved to significantly reduce the spread of the SARS-CoV-2 virus. Over the course of the pandemic, however, environmental researchers began taking note of the improper disposal and increased waste of face masks and other pandemic-associated PPE throughout a wide range of environments. This study assessed metrics of degradation of black and blue surgical face masks in two environments (indoor and outdoor) over 16 weeks based on four metrics: FTIR spectral analysis and carbonyl index, dry weight measurements, photometric light transmission, and individual microfiber counts. Overall, microfibers counted in seawater and from freshwater rinses were the best metrics used to measure degradation: microfiber counts in seawater significantly increased and microfibers counted from freshwater rinses significantly decreased over the course of the study. The results from the other three metrics were inconclusive as measures of degradation. Black outdoor masks released 45% more microfibers than blue outdoor masks, and black masks in total released 49% more microfibers than both types of blue masks. Logarithmic models generated for blue and black mask microfiber release show that microfiber release rate begins to plateau after approximately 100 years but does not reach a maximum, even after 500 years. Plastic pollution is already a significant environmental challenge and understanding how a global pandemic contributes to it will be crucial for developing conservation strategies in the future.

Keywords: Plastics, pollution, COVID-19, pandemic, polymers, degradation

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Introduction

The evolution of humanity has been centered around waterways. Oceans cover approximately seventy percent of Earth's surface, and early civilizations who had access to a river, estuary, lake, or ocean became wealthy and powerful through irrigation for farming, commerce, and military might on land and at sea. The industrial revolution brought about unprecedented advancements in technology, and humanity's quality of life rose with it. However, the world's natural environment has since been under threat. Increased industrial production has caused a dramatic rise in carbon dioxide emissions, which eventually sinks into the oceans. According to the United Nations (2017), the world's oceans support between 500,000 and 10 million marine species, and marine phytoplankton accounts for 50 percent of the planet's oxygen. With increased carbon dioxide levels in the ocean, marine biodiversity has been under threat from ocean warming and acidification. Plastic waste has also been a major player in the threat to our oceans, and it has only grown since 2020.

The COVID-19 pandemic has been the largest major global public health crisis in the last century, and several mitigation methods were implemented by federal and local governments across the world. Due to its high contagiousness and transmissibility, businesses were advised to completely shut down operations early on, and stay-at-home orders as well as social distancing guidelines, travel restrictions and personal hygiene advisements were established to stop the spread of the SARS-CoV-2 virus. Concurrently, the demand for personal protective equipment (PPE) grew exponentially and will likely not slow down for some time (Chowdhury et al. 2021). As stay-at-home orders were lifted and economies began reopening over time, face coverings became mandated on public conveyances (airplanes, busses, ferries, etc.) by the Centers for Disease Control and Prevention (CDC) in order to control the aerial dispersal of SARS-CoV-2-containing droplets (Department of Health and Human Services, 2021). Around the same time, states were given the power to lift or enforce mask mandates, but businesses in states where mandates were lifted were still able to choose whether patrons were required to wear masks inside (Thorbecke, 2021).

In the United States and many parts of the world, single-use face masks had primarily only been used in hospital settings to prevent occupational hazards. However, due to the increased demand for PPE at the beginning of the pandemic, companies worldwide began mass-producing and distributing surgical face masks. In 2020, the production rate of surgical face

masks was estimated to be between 2.4 and 54 billion (Eurostat 2021; Ching & Phan 2020; Patrício Silva et al. 2021; Saliu et al. 2021). The Japanese Ministry of Economy, Trade and Industry (METI) revealed that an order of 600 million surgical face masks per month was secured in April of 2020 (Fadare & Okoffo, 2020; METI 2020), and in June of 2020 alone, China's production rate was at 200 million per day (Aragaw 2020), which is more than 20 times the amount produced in February of 2020 (Saliu et al. 2021). The World Wildlife Fund (2020) estimated that just one percent of face masks produced during the COVID-19 pandemic could contribute 30,000-40,000 kilograms (kg) of waste per day (Chowdhury et al. 2021).

Although the effectiveness of face masks against the spread of COVID-19 varies by brand and material composition, they are generally composed of multiple layers of non-woven fabrics and plastic polymers. Face masks are constructed by combining a waterproof and colored outer layer, an inner layer for direct droplet absorption, and a middle layer that acts as a primary filtration device (Morgana et al. 2021). Heat, chemical and mechanical means are used to fuse different filaments together to produce non-woven textiles. The middle layer is a melt-blown filter produced by electrospinning and conventional fabrication, where the melted polymer is pushed through tiny pores by a high speed, blowing gas (Fadare & Okoffo, 2020). Polyurethane, polystyrene, polyethylene, and polyester have been detected in many types of face masks, and polypropylene is the foremost polymer found in surgical face masks (Aragaw, 2020).

Plastic polymers are made up of long hydrocarbon chains with a relatively high average molecular weight (Law, 2017). Most, but not all, plastic polymers are derived from fossil fuels and enhanced with additives such as UV stabilizers, flame retardants and coloring agents (Law, 2017). Polypropylene has been used to mass-produce surgical face masks because it is relatively cheap and easy to process due to its low melt viscosity (Morgana et al. 2021). Different plastic polymers exhibit different degradation behaviors and suffer varying fates when exposed to the marine environment. For example, polyethylene terephthalate (PET), which has been deemed as a "safe and affordable" polymer, has a density of 1.37-1.45 g cm^{-3} (Issac & Kandasubramanian, 2021), causing it to sink and become more prevalent in the benthic realm. Polyethylene (PE) and polypropylene (PP), on the other hand, have densities of 0.920 g cm^{-3} and 0.905 g cm^{-3}, respectively. Seawater has a density of approximately 1.03 g cm^{-1}, therefore, lower density polymers such as PE and PP will be found in surface waters (De-La-Torre & Aragaw, 2021).

Since their development in 1907 with the creation of Bakelite and, subsequently, the economic challenges of World War 2, synthetic plastics have become a ubiquitous staple of modern life. The production of consumer goods has become reliant on plastics due to their affordability, light weight, and durability (Sigler, 2014). Packaging products, household electronics, clothing and automobiles are among a long list of examples of goods that are made with synthetic plastics. As of 2014, approximately 280 million tons of plastic materials were made annually (Shaw & Sahni, 2014), and much of it eventually ends up in either landfills or the oceans. Despite existing for over one hundred years, plastic pollution in the environment has only been noted as a significant concern in the last three to five decades (Law, 2017; Sigler, 2014). The utilization of surgical face masks and other single-use PPE has proven to be an effective public health safety net against COVID-19, but the exponential increase in production has led to environmental challenges, with improper disposal being a significant factor.

Figure 1: Used face mask improperly discarded in Plantation, FL, USA. Photo taken by Christopher Mayer (2022).

Single-use face masks have been reported as littered on city streets, parking lots, water runoff pathways, beaches and more. Along with other single-use plastics, surgical face masks were already a component of global plastic waste from the health-care industry. Ingestion of common consumer goods and entanglement in abandoned fishing gear are among the most detrimental impacts to marine life, but plastics can also be carriers of toxicants that can have adverse effects to life across all trophic levels. Microplastics have the potential to accrue

hazardous organic chemicals such as DDT and other synthetic additives, release organic contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), and some researchers have suggested classifying them as hazardous waste (Eriksen et al. 2014; Teuten et al. 2009). The polymeric bonds of synthetic plastics make them resilient to biodegradation in the environment, but they undergo physical, chemical and photodegradation processes which reduce primary plastics into smaller fragments, or microplastics, over time scales of years to decades.

Depending on the polymer, microplastics typically range between <1 millimeter (mm) and 10 mm in length. As these microplastics break down, the risk of exposing living organisms at different levels of the food chain to chemical additives and absorbed contaminants increases, though the adverse effects are still not well understood (Law & Thompson, 2014; Issac & Kandasubramanian, 2021). Additive-free plastics are in production today, and while they provide more of a safeguard against chemical pollution, their physical existence in the ocean poses a threat of its own. To date, reports of nearly 700 species of aquatic organisms, including sea turtles and crustaceans, suffering adverse health effects due to microplastic ingestion have surfaced (Marn et al. 2020). The prevailing issue with microplastic ingestion, however, is that there could be an exponentially greater number of species across the oceans being adversely affected that have yet to be discovered, providing a substantial knowledge gap in how plastic waste affects the marine environment.

The exponential increase in PPE production and public use during the COVID-19 pandemic has raised new concerns on single-use face masks as a potential new source of micro and/or nano plastic pollution in marine and terrestrial environments. Morgana et al. (2021) conducted an experiment in which they measured the short-term shear stress tolerance of surgical face masks and their associated microplastic release by using a kitchen chopper with a rotating blender blade. The masks were subjected to five shear stress times ranging from 1 to 120 seconds to measure the percent of weight lost in milligrams (mg). Four replicates were used for each time, and the energy density (kJ/L) of the kitchen chopper increased with time. Optic stereomicroscopy and flow cytometry were used to quantify the microplastic released from each shear stress test. They found that the number of microplastics released from the masks directly correlated to the time they were exposed to the shear stress test and the energy density of the treatment (kJ/L), and the increase in released microplastics followed a sigmoidal curve. Flow

cytometry used in this study showed that the highest number of released microplastic particles were between 0.1-0.5 µm and <0.1 µm.

Chowdhury et al. (2021) estimated the PPE waste from coastal populations in 46 countries. The researchers assessed face mask acceptance and use in these countries and compared it to the waste management systems already in place. Daily face mask usage was calculated by multiplying data from each country's coastal population and coastal population percentage, and mask acceptance provided by the Encyclopedia of Coastal Science (as cited in Chowdhury et al. 2021) and various international surveys. Annual face mask usage was calculated by multiplying the daily face mask usage values by 365. It was found that overall, 2.37 million tons of mismanaged plastic waste from face masks in the analyzed countries, with Indonesia at the forefront contributing 17.46% of plastic waste generation. The researchers determined that lower-income countries were responsible for a higher percentage of mismanaged waste than upper-middle-class and high-income countries. Table 1 highlights some of the mismanaged waste data from Chowdhury et al. (2021).

Table 1: Estimated annual face masks waste data (in tons) from 12 of 46 countries analyzed (Chowdhury et al. 2021). "SM" stands for surgical masks.

Country	Plastic waste from SM	Plastic waste from N95	Total plastic waste generation	Mismanaged waste	Debris upper estimate	Debris lower estimate
Bangladesh	42,205	25,709.9	67,996	65,786.13	26314.45	9867.91
China	90,567	157,349	145,916	37,573.37	15,029.348	5636
Indonesia	256,865.1	156,972	413,837	250,371.39	100,148.553	7555.71
India	100,572.1	61,462,35	162,034.45	128,007.22	51,202.88	19,201.08
USA	59,604.5	36,427	96,031.5	2871.34	1148.53	430.70
Canada	2211.9	1350.5	3562.4	71.25	28.5	10.68
Argentina	10,205.4	6234.2	16,439.6	4044.14	1617.66	606.62
Brazil	33,459.55	20,447.3	53,906.85	13,589.92	5435.96	2038.48
Finland	2025.75	1237.35	3263.1	65.60	26.24	9.84
Denmark	5934.9	3175.5	9110.4	184.03	73.61	27.61
Netherland	14,749.65	9026.45	23,776.1	475.52	190.21	71.32
Belgium	8492.5	5464.05	14,406.55	613.72	245.48	92.05

As a significant new source of plastic pollution, understanding how long the plastic polymers associated with face masks remain in the marine environment will be crucial for ecosystem health assessments and further research into the adverse effect plastic products have on marine life. The rate of nano plastic release from microplastics in aquatic environments, the long-term fate and degradation rate of improperly discarded face masks in the natural

environment, and whether disposable face masks can be properly categorized as a new source of microplastic pollution are unknown. To begin to address these knowledge gaps, the current study evaluated the physical and chemical degradation of surgical face masks in a relatively controlled marine environment and laboratory setting. Three main research questions were posed: First, do black and blue surgical face masks degrade at the same rates in seawater? Second, does exposure to sunlight increase degradation rates in surgical face masks? Third, what is the best method of measuring degradation in surgical face masks? To answer these questions, the degradation rate of black and blue surgical face masks in seawater under two exposure conditions (indoor and outdoor) was assessed using four metrics [dry weight, light transmission, microplastic release and carbonyl index (CI)]. Black and blue surgical face masks were chosen because they were the cheapest and most common face coverings available to the public, and thus more likely to be improperly discarded.

While this study only focused on two types of face masks, the main goal was to provide a unique perspective on the pandemic and the existing plastic pollution problem, and to compare metrics of plastic degradation. Examining the rates at which surgical face masks degrade by quantifying microplastic release and monitoring their structural integrity over time is a starting point in comprehending the ramifications a global pandemic can have on the natural world, how a modern public health crisis of this magnitude contributes to the already mounting plastic pollution issue, and provides guidance for researchers and policy makers so that they may develop effective strategies to reduce the harm that littered plastics bring to our oceans.

Materials and Methods

Experimental design

Face mask degradation was measured by changes in the dry weight in grams (g), carbonyl index (CI), counts of released microfibers, and the amount of light transmitted through each mask in watts per square meter (W/m^2) over time. Ten brand-new black and blue masks ordered from Amazon were placed in separate Pyrex 2L glass bottles, which were filled with sterile, artificial seawater mixed in the coral nursery at Nova Southeastern University's Halmos College of Arts and Sciences. A total of forty (n=40) 2L bottles were used; twenty (n=20) bottles were kept inside the Marine Toxicology Lab at ambient temperature with no exposure to

sunlight, and twenty (n=20) bottles were left outside on a wooden rack (figure 2) for the duration of the experiment. Each bottle was manually shaken by being vigorously inverted fifteen times once per day, Monday through Thursday of each week. On Wednesday of each week, one bottle filled with black masks and one bottle filled with blue masks from both the outdoor and indoor settings (n=4) was removed from the study and taken to the Sediment Lab for processing. This sampling was performed once per week for the first four weeks, and once every other week for the remainder of the experiment. The 2L of seawater from each glass bottle were divided into 500 mL aliquots and distributed among four different beakers. Temperature (°C) and salinity (ppt) of the seawater in each beaker (1-4) was measured using a YSI Pro1030 instrument, and the water in each beaker was filtered through a MF-Millipore filter paper (pore size – 0.45 μm). This process was carried out for each 2L bottle on every sampling day.

Figure 2: Bottles in the outdoor group exposed to natural conditions (n=20).

After YSI measurements were taken, each mask was removed from its respective bottle, rinsed in 500 mL of fresh tap water four times to remove salt residue, and placed under a fume hood to dry overnight. The freshwater used to rinse each mask was poured into separate 1L

bottles, filtered, and examined to further quantify the microplastics released in the degradation process. This step was added to account for the potential plastics lost during the fresh tap water rinsing process. After rinsing, the masks were then dried in a fume hood; due to space restrictions, two fume hoods were used to dry the masks. The indoor groups of both colors were left in the Sediment Lab, and the outdoor groups of both colors were taken to the Marine Toxicology Lab (Figure 3). After the masks were dried overnight, they were all placed into individually labeled 1 quart Ziploc bags and brought to the Marine Toxicology Lab for light transmission measurements and the Coral Histology Lab for dry weight measurements.

Figure 3: Black and blue outdoor masks drying in the fume hood of the NSU Marine Toxicology Laboratory.

Light Transmission and Dry Weight Measurements

A Solar Light PMA2100 Datalogging Radiometer equipped with a photosynthetically active radiation (PAR) sensor was used to assess levels of light transmission through all mask samples underneath an Ecotech Radion XR30 GS Pro light. The PAR sensor was placed at a distance of 42.545 cm from the center of the light and a baseline reading was established. Each mask was then taken out of its respective Ziploc bag, peeled open and draped face-up, completely covering the PAR sensor (Figure 4A). Each mask was returned into its respective Ziploc bag after individual measurements were taken. Upon completion of measuring light transmission, the masks were taken to the Coral Histology Lab for dry weight measurements. Each mask was removed from its respective Ziploc bag and placed in a five-hundred mL plastic beaker, which was pre-tared on the balance (Figure 4B). The weight of the masks was measured in grams (g) to the ten-thousandths place with an analytical balance.

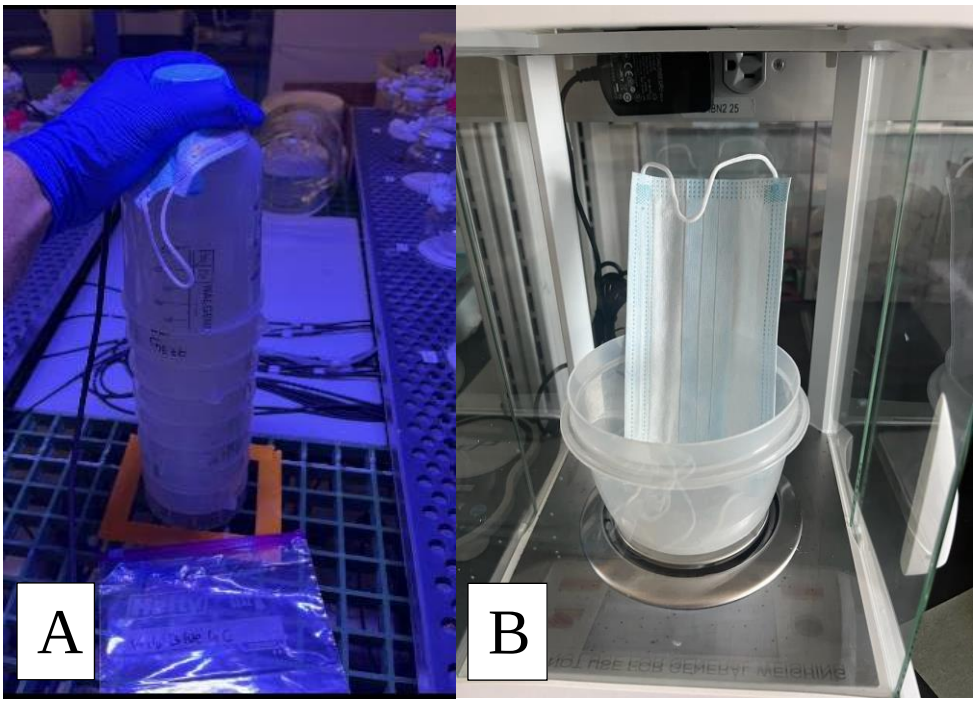

Figure 4: A) Experimental procedure for obtaining light transmission readings (W/m^2). Masks were peeled open and securely draped over the PAR sensor, which was rested on top of the nine-beaker stand. B) Experimental procedure for obtaining dry weight measurements (g). Masks were weighed in a pre-tared cup inside of a (brand) analytical balance.

ATR-FTIR Spectroscopy

Polymer identification was performed using attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) spectroscopy at NSU's Main Campus (Davie, FL, USA). ATR-FTIR analysis was used to obtain the carbonyl index (CI) of each mask, which provides insight into how the absorption bands and structural composition of the polymers that compose the surgical face masks changed over time. The base and crystal of the ATR-FTIR machine was cleaned with acetone and dried with a Kimwipe before measurements were taken. Each mask was then removed from its respective Ziploc bag and placed underneath the crystal, which was gently tightened (Figure 5). Readings were taken of both the inner and outer layers of each mask and measured in the wavenumbers per centimeter (cm^{-1}) range of 400 cm^{-1} and 4000 cm^{-1}. The CI was obtained using the specified area under band (SAUB) method as described in Almond et al. (2020). The ratio between the integrated absorbance bands of the carbonyl (C=O) peak (1,650 cm^{-1} - 1,850 cm^{-1}) and methylene (CH_2) peak (1,420 cm^{-1} -

1500 cm^{-1}) was used to calculate the CI using the following equation from Almond et al. (2020), hereafter referred to as Equation 1:

Equation 1:

$$\text{Carbonyl Index} = \frac{Area\ under\ band\ 1{,}850{-}1{,}650\ cm^{-1}}{Area\ under\ band\ 1{,}500{-}1{,}420\ cm^{-1}}$$

Figure 5: ATR-FTIR analysis of a blue surgical face mask at the NSU Main Campus.

Released Microfiber Quantification

The sterile seawater from the 2L Pyrex glass bottles and the fresh tap water from the procedural blanks were filtered with an electric pump in the Sediment Lab. Gloves and a lab coat were worn to prevent contamination, and the magnetic cup used to hold the water was rinsed with deionized water after each sample had completed filtration. Pictures of each 0.45µm pore-sized MF-Millipore filter paper were taken using a Canon TG6 camera and analyzed with the manual cell-counting function in ImageJ.

Statistical Analysis

GraphPad Prism 10 software was used for all statistical analyses. Linear regressions (α=0.05) were used to evaluate the effect of time on all four continuous response variables. Nonlinear regression was also used for the freshwater rinse data. Logarithmic models were generated in Microsoft Excel to predict microfiber degradation from a single mask over longer

time scales. To generate these models, the total number of microfibers counted in this study each week from each bottle type was divided by 10 since each 2L bottle in this study contained 10 masks. Figure 6 shows a graphical representation of the experimental design.

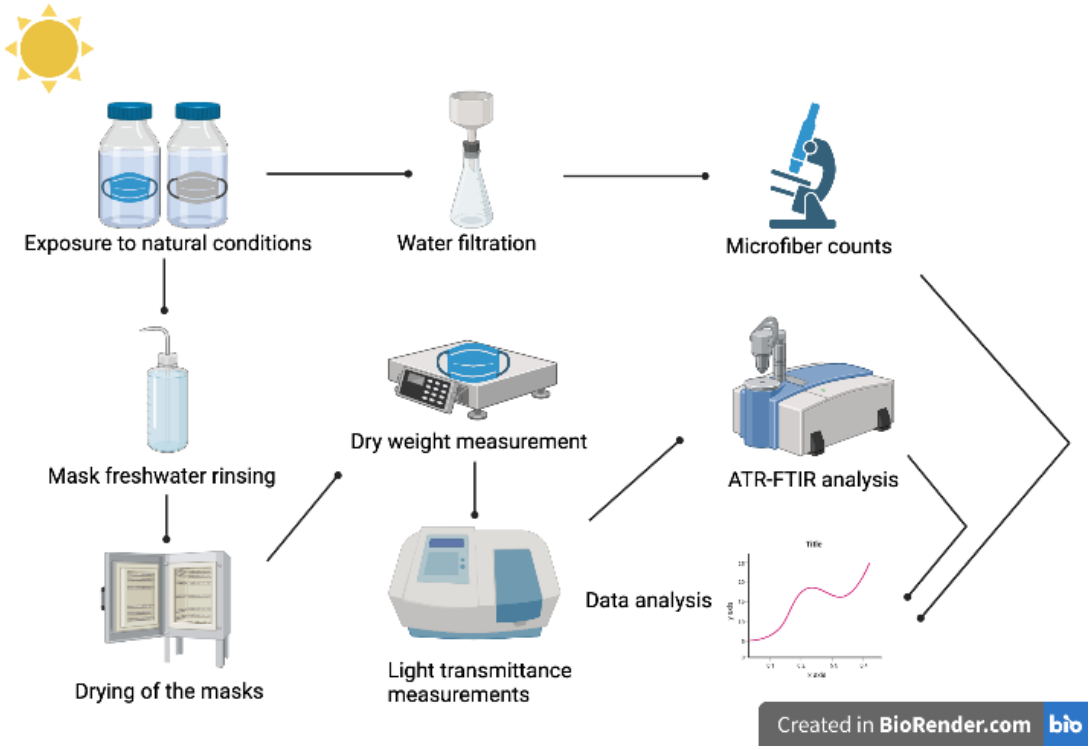

Figure 6: Experimental design and sampling procedure.

Results

Light Transmission

Overall, there was no significant change in light transmission measurements over time. The light measurements of the black indoor masks stayed relatively the same throughout the duration of the experiment (linear regression, R^2= 0.0005533, p=0.9453). Black outdoor masks saw a gradual increase in light transmission, but the results were not statistically significant (linear regression, R^2=0.04204, p=0.0723). Blue outdoor masks did not experience a significant increase in light transmission (linear regression, R^2=0.02338, p=0.1108), however, there was a significant decrease in light transmission in blue indoor masks over time (linear regression, R^2=0.05341 p=0.0151). In comparing the blue and black outdoor masks to each other (linear regression), black outdoor masks had a significant increase in light transmission (R^2=0.3152,

p=0.0317) and blue outdoor masks did not (R^2=0.02338, p=0.1108). Figure 7 shows the interactions between mask types over time.

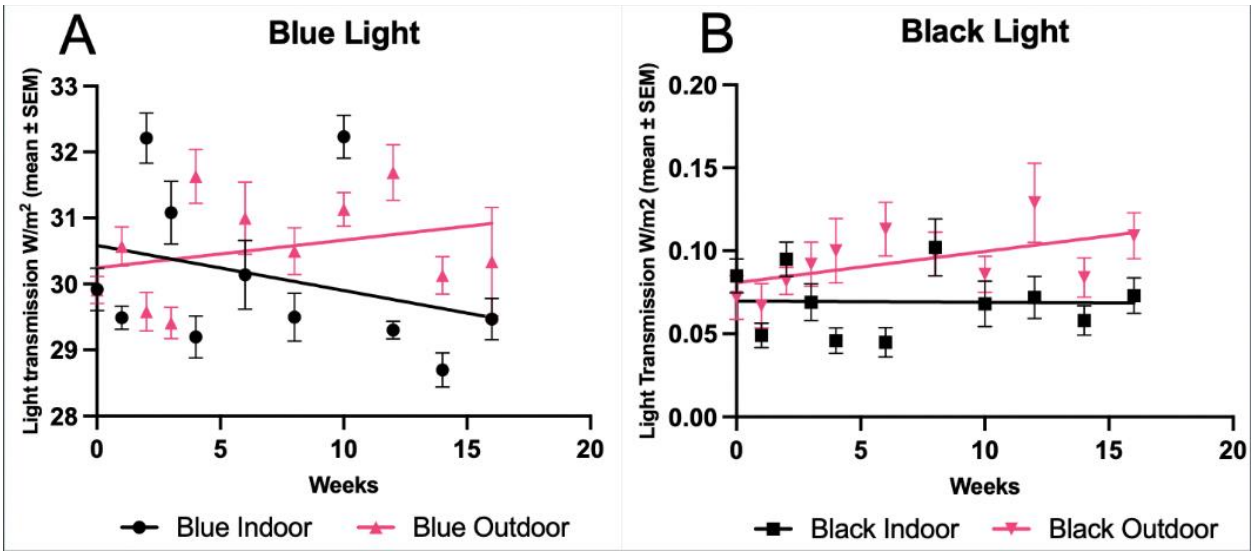

Figure 7: A) Mean light transmission (±SEM) of blue indoor and outdoor masks over time. B) Mean light transmission (±SEM) of black indoor and outdoor masks over time.

Dry Weight

Significant changes in dry weight over time were observed for black indoor masks, blue outdoor masks, and black outdoor masks, but not for blue indoor masks (Figure 8). The dry weight of blue indoor masks slightly increased but this change was not significant over the duration of the experiment (linear regression, R^2=0.03368, p=0.0550). Black indoor masks decreased in dry weight significantly (linear regression, R^2=0.4451, p<0.0001), as did the blue outdoor masks (linear regression, R^2=0.1109, p=0.0004). However, the black outdoor masks showed peculiar behavior. In weeks one and two, the mean dry weight of the black outdoor masks dropped drastically but increased in week three and then stayed relatively constant throughout the remainder of the experiment (linear regression, R^2=0.2888, p<0.0001).

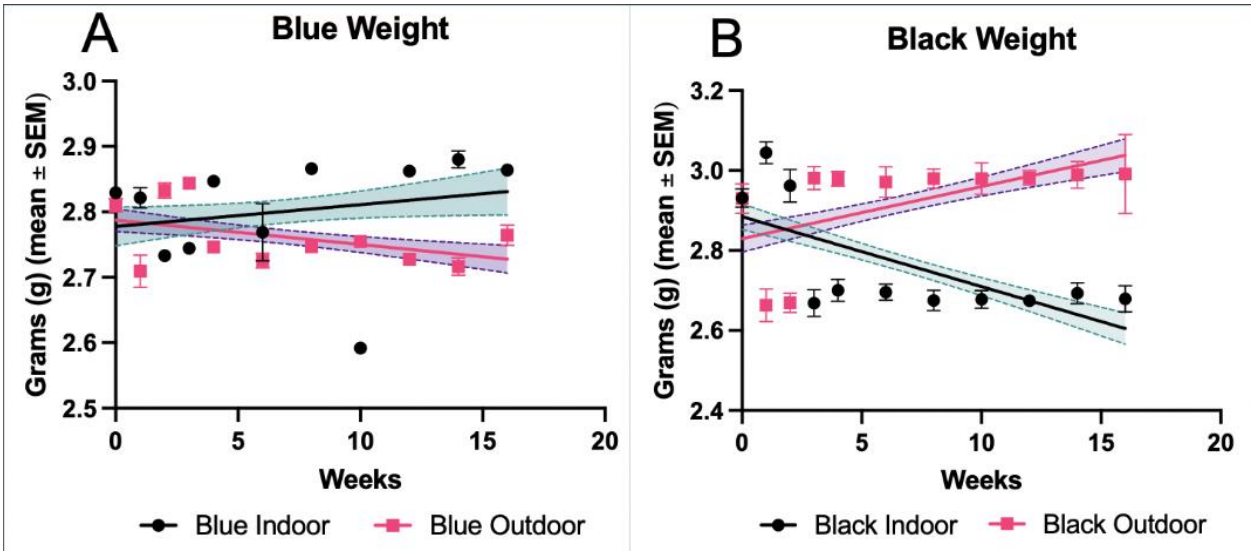

Figure 8: A) Mean dry weight (±SEM) of blue indoor and outdoor masks with 95% confidence intervals (shaded). B) Mean dry weight (±SEM) of black indoor and outdoor masks with 95% confidence intervals (shaded).

Microfiber Counts

In total, across all four mask types and throughout the duration of the experiment, a total of 159,031 microplastic fragments were counted in the seawater and freshwater. Black outdoor masks had the highest count of released microfibers with 54,975 pieces, or 34.57% of the grand total, and black indoor masks were responsible for 31.47% of the total with 50,047 released microfibers. Blue outdoor masks accounted for 19.20% of microfibers released throughout the experiment with 30,539 fibers, and blue indoor masks released 23,470 fibers, 14.75% of the total. A total of 32,001 microfibers were counted from the freshwater rinses of the masks. Black outdoor freshwater rinses had the highest microfiber release count of each type at 12,525 (39.1%), followed by black indoor freshwater rinses with 8,355 fibers (26.1%). Blue outdoor and indoor freshwater rinses accounted for 6,626 (20.7%) and 4,495 (14.1%) fibers, respectively.

Microfiber counts from the seawater in the 2L bottles significantly increased for all four mask types over the 16-week duration of the experiment (Figure 9). Black outdoor masks (linear regression, R^2=0.8044, p=0.0004) released fewer microplastics than black indoor masks (linear regression, R^2=0.6777, p=0.0034) in week 1, but overtook the black indoor type in week 2 and beyond. Blue outdoor masks (linear regression, R^2=0.8914, p<0.0001) also released fewer microplastics than blue indoor masks (linear regression, R^2=0.8344, p=0.0002) in week 1 of the experiment but released more every other week of the experiment except for week 8.

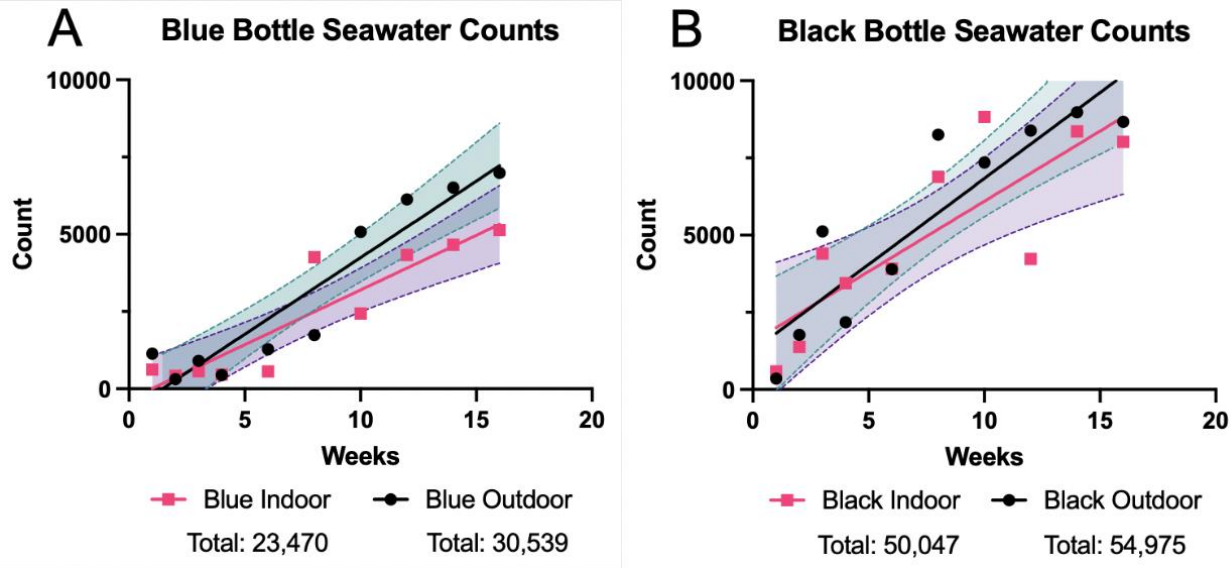

Figure 9: A) Microfiber counts of blue outdoor and blue indoor masks from 2L of seawater with 95% confidence intervals. B) Microfiber counts of black outdoor and black indoor masks from 2L of seawater with 95% confidence intervals.

Microfiber counts decreased significantly for the freshwater rinses of each mask type over the duration of the experiment (Figure 10). Black outdoor mask freshwater rinses (linear regression, R^2=0.6364, p=0.0057) saw a large reduction in the number of fibers counted after week 2 and remained relatively constant throughout the remainder of the experiment. Black indoor mask freshwater rinses (linear regression, R^2=0.7525, p=0.0011) showed a slight increase in microplastic released between weeks 1 and 2 before a strong decrease between weeks 2, 3, and 4. Released microplastics in this category remained relatively constant after week 4. Blue outdoor mask freshwater rinses (linear regression, R^2=0.5445, p=0.0148) had a large decrease in released microfibers after week 2 and leveled off after week 3. Microfibers released from blue indoor mask freshwater rinses (linear regression, R^2=0.4322, p=0.0389) decreased drastically after week 1, kept decreasing between weeks 2, 3 and 4, slightly increased in week 5, and then decreased again and remained relatively constant for the remainder of the experiment.

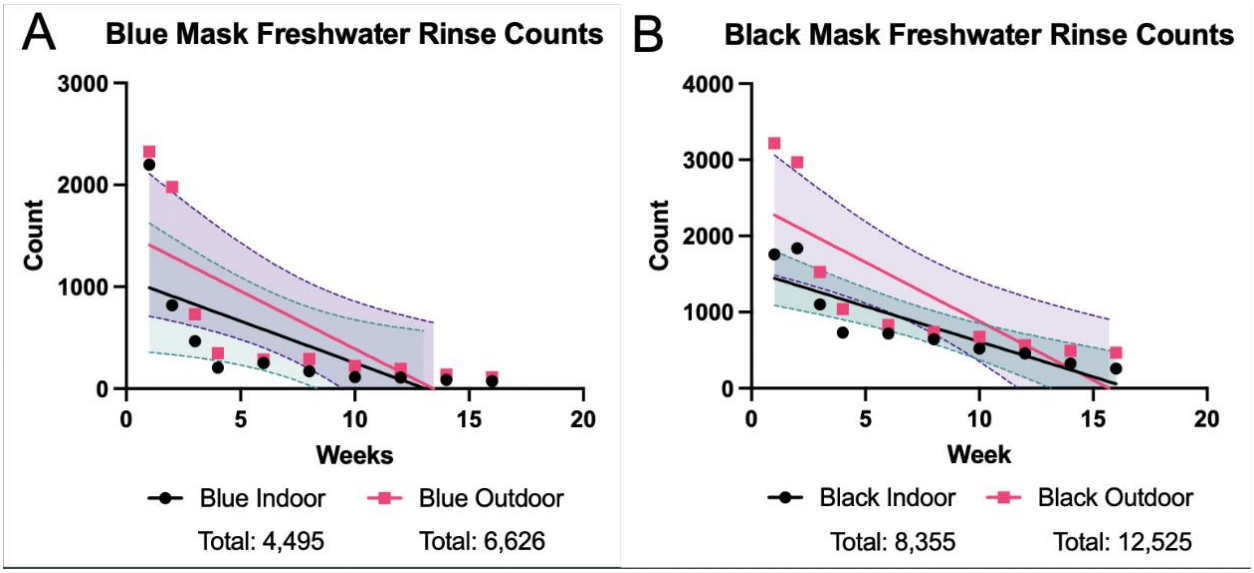

Figure 10: A) Microfiber counts from blue freshwater rinses with 95% confidence intervals. B) Microfiber counts from black freshwater rinses with 95% confidence intervals.

Logarithmic models were generated to predict microfiber counts over a long-term scale, with 500 years chosen as the assumed maximum degradation time (Figure 11). Microfiber release begins to level off around 40-50 years but continues to gradually increase over the 500-year span. The y-intercepts of the equations show that in one-year, blue outdoor masks would release 854.82 microfibers, blue indoor masks would release 640.92 microfibers, black outdoor masks would release 1,281.80 microfibers and black indoor masks would release 1,217.40 microfibers. The R^2 values of these models are 0.6690, 0.6852, 0.8494 and 0.8896, respectively.

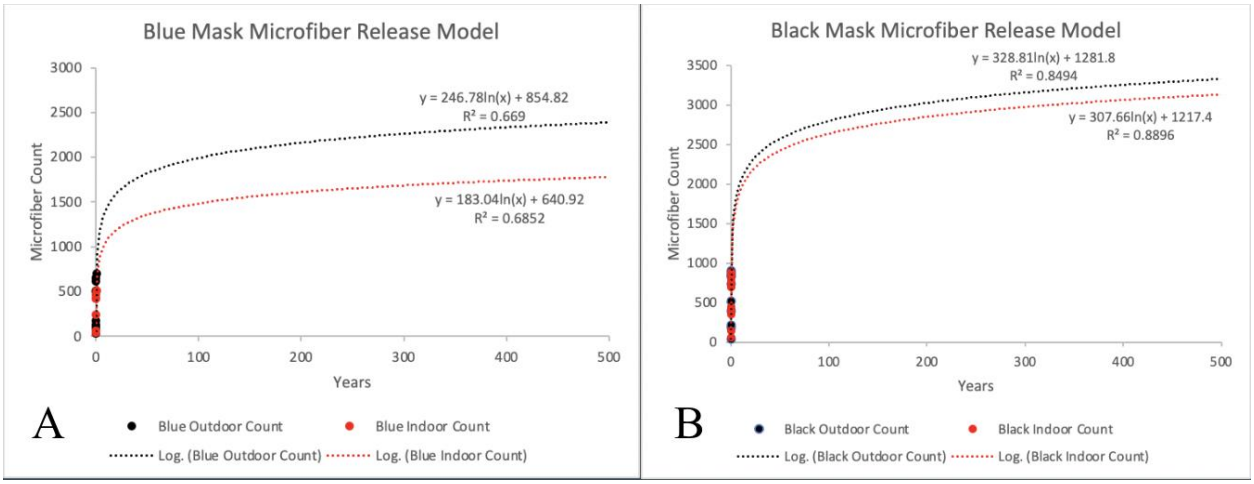

Figure 11: Logarithmic models of microplastic release in indoor and outdoor settings over a 500-year period for A) blue indoor and outdoor surgical face masks and B) black indoor and outdoor surgical face masks.

ATR-FTIR Spectroscopy – Carbonyl Index

Samples from weeks 1-6 were lost, so only results from sampling weeks 8-16 were considered. Overall, CI decreased across the inner and outer layers of all four outdoor mask types (Figure 12). The inner layer of black outdoor (linear regression, R^2=0.2284, p=0.0004), inner layer of blue outdoor (linear regression, R^2=0.2665, p=0.0001), and outer layer of blue outdoor (linear regression, R^2=0.2515, p=0.0002) masks all had statistically significant decreases in CI. The decrease of CI in the outer layer of black outdoor (linear regression, R^2=0.06325, p=0.0781) masks, however, was not statistically significant.

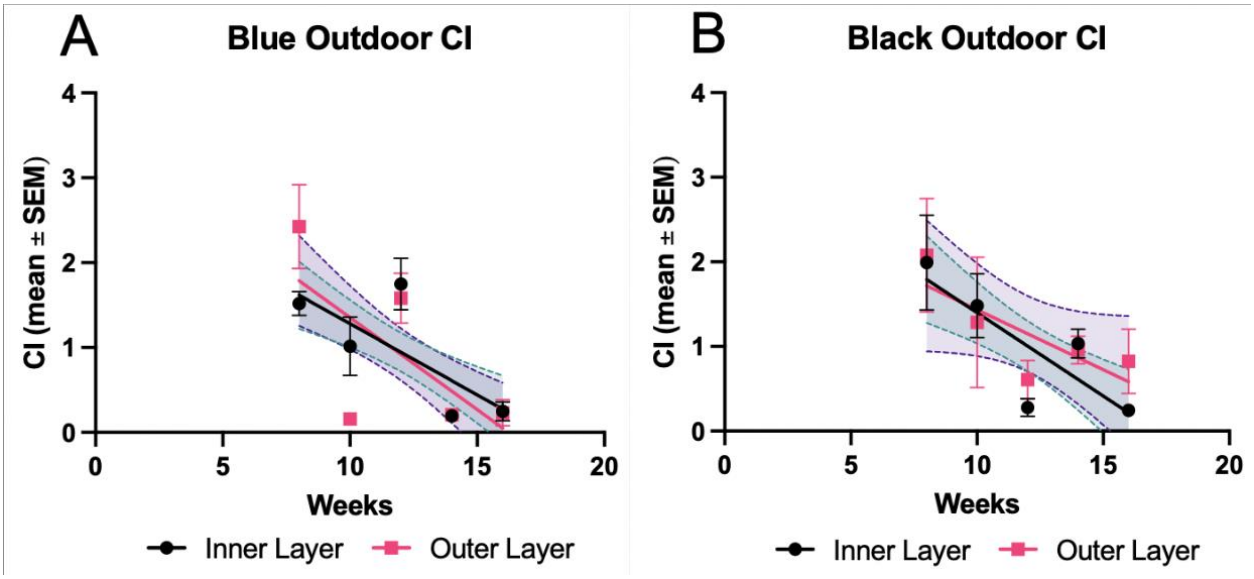

Figure 12: A) Carbonyl index of the inner and outer layers of blue outdoor masks from weeks 8-16 with 95% confidence intervals. B) Carbonyl index of the inner and outer layers of black outdoor masks from weeks 8-16 with 95% confidence intervals.

CI significantly decreased in the inner (linear regression, R^2=0.2147, p=0.0007) and outer (linear regression, R^2=0.09143, p=0.0328) layers of black indoor masks, but not in blue indoor masks (inside: simple linear regression, R^2 = 0.0001571, p = 0.9312; outside: linear regression, R^2=0.000809, p=0.8379).

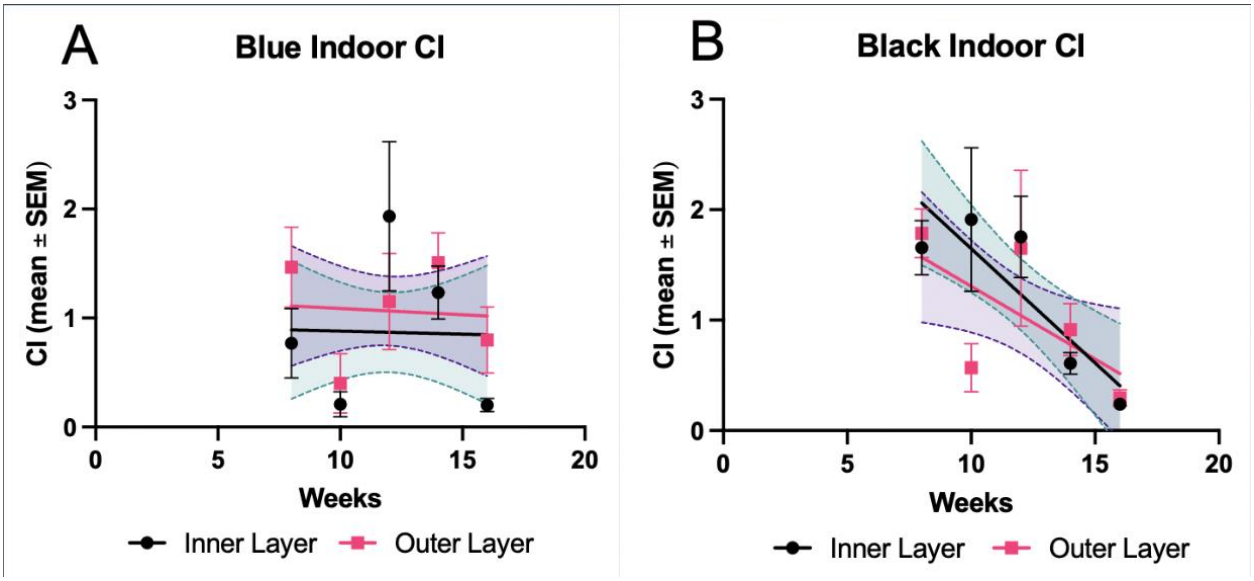

Figure 13: A) Carbonyl index of the inner and outer layers of blue indoor masks from weeks 8-16 with 95% confidence intervals. B) Carbonyl index of the inner and outer layers of black indoor masks from weeks 8-16 with 95% confidence intervals.

Results Summary

The overall results of the study, showing relative increases and decreases in the metrics used, along with indicators of specific statistical significance, and are summarized in Table 2.

Table 2: Summary of results. Green, upward arrows represent increases over time. Red, downward arrows represent decreases over time. * = statistical significance.

	Dry Weight	Light Transmission	Seawater Microfiber Count	Mask Rinse Microfiber Release	Inner Layer CI	Outer Layer CI
Blue Indoor	↑	↓ *	↑ *	↓ *	↓	↓
Blue Outdoor	↓	↑	↑ *	↓ *	↓ *	↓ *
Black Indoor	↓ *	↓	↑ *	↓ *	↓ *	↓ *
Black Outdoor	↑ *	↑	↑ *	↓ *	↓ *	↓ *

Discussion

The goals of this study were to examine the degradation rates of black and blue surgical face masks under controlled environmental conditions to better understand the potential effect of the COVID-19 pandemic on the marine environment and to compare four metrics used to measure degradation in plastics. Several studies since the onset of the COVID-19 pandemic have recognized surgical face masks as a novel environmental threat, but this study is the first to experimentally compare these four metrics in a 16-week study. There was variation in the effectiveness of each metric as an applicable measurement of degradation, but some significant results were obtained.

Light Transmission

This study was the first attempt to use light transmission with a PAR sensor as a metric of degradation in black and blue surgical face masks. It was expected that the black indoor masks would not show much variation in light transmission over time due to the color black's high light absorption, but it was unexpected that light transmission significantly decreased in blue indoor masks and did not significantly increase in either of the outdoor groups. UV irradiation has been shown to cause changes in the structure of surgical face masks that affect micro and nano plastic release (Liang et al. 2023; Weinstein et al. 2016), but no other study has reported on how long-term UV exposure affects light transmission through the masks. As this study began at the end of the summer in South Florida, it was thought that exposure to high UV levels for several months would degrade both groups of outdoor masks to an extent that would result in statistically significant differences in light transmission in at least one of the two groups. The R^2 values for black indoor, blue indoor, and blue outdoor masks in the current study (0.0005533, 0.05341, and 0.02338, respectively) showed that exposure time had very little differential impact on the variation in light transmission measurements.

Although the light transmission through black and blue outdoor masks increased over time, it is possible that biofilm accumulation could explain why the results of the present study were statistically insignificant. It is also possible that photo-oxidative and photolytic reactions caused by light and UV radiation could have played a strong role in the results obtained in the first few weeks of this study before biofilms would have formed. However, this does not explain the significant decrease in light transmission in blue indoor masks. If biofilm accumulation

played a role in the increase or decrease of light transmission in any type of mask, it would be expected that there would be a stronger effect on outdoor masks left in natural conditions rather than inside of a laboratory setting. It is also possible that salt residue that was not adequately washed from any type of mask could have impacted the significance of the increases in light transmission of the outdoor masks. Light transmittance, or, the amount of light absorbed, reflected, or scattered by a substance, may be a better metric to use than light transmission in future studies. The amount of light that a particular substance absorbs, scatters, or reflects could be a better indication of polymer embrittlement if the amount of transmittance decreases over time. If one were to question how degraded a derelict face mask is, the results of the analyses performed on the data suggest that light transmission alone may not be a viable metric.

Dry Weight

It was unexpected that some types of masks experienced an increase in dry weight and others decreased in dry weight over time. The observed change in dry weight of blue outdoor masks over time was expected, but the dramatic initial decrease and subsequent increase in the dry weight of black outdoor masks was surprising. Weinstein et al. (2016) reported biofilm accumulation beginning on polypropylene strips after 2 weeks of open environmental exposure and a 33.5% increase in the dry weight of these strips after 32 weeks due to biofilm accumulation and other organisms that encrusted their samples. On the other hand, the high-density polyethylene strips in the study by Weinstein et al. (2016) did not increase significantly over the course of their experiment, even with the accumulation of biofilm. The R^2 values for black indoor, black outdoor, and blue outdoor masks (0.4451, 0.2888, and 0.1109, respectively) showed that time had a significant impact on the variation in dry weight measurements in these groups over time, but it does not explain the sudden decrease and increase in values of the black outdoor masks between weeks 0 and 1 and weeks 3 and 4.

It is possible that rusting and/or biofilm accumulation in the outdoor masks could have affected the dry weight measurements of the black outdoor masks. Both types of outdoor masks were left outside in closed containers, but the 2-L glass bottles were not air-tight, so biofilm accumulation cannot be ruled out. It is also possible that mask coloration is somehow associated with biofilm accumulation, but, as of now, it is unclear as to why the changes in dry weight of the blue outdoor masks did not occur in the same manner as the black outdoor masks. Weinstein

et al. (2016) reported that previous studies such as Gutow et al. (2016) have documented mucus rich in polysaccharides produced by seaweeds adhering to microplastics, supporting the theory that biofilm formation may have influenced the dry weight measurements in this study.

Dry weight has been used as a metric of degradation in surgical face masks in other studies, but only after significant manipulation of the mask structure. For example, Morgana et al. (2021) cut the ear loops off their masks, removed the middle filtration layers, and subjected them to blending in a kitchen chopper for various durations before weighing. The surgical face masks used in this study were not manipulated in any way before treatment and significant changes in dry weight were not expected in the black or blue indoor masks. The results obtained in this study, however, do not allow accurate degradation predictions to be made by dry weight alone. It was expected that there would be an inverse relationship between dry weight and light transmission measurements. Specifically, it was expected that as dry weight decreased, light transmission measurements would increase. Biofilm accumulation likely skewed the results obtained, and the conclusion that dry weight should not be used as the only metric of degradation is supported by Morgana et al. (2021). It could be possible that, after three weeks in the environment, rusting and/or biofilm accumulation stops on black surgical masks and prevents degradation, which could explain why the dry weight of the black outdoor masks remained relatively the same after week 3 of the experiment.

Microfiber counts

Microfiber release from the outdoor groups behaved as expected over the 16-week duration of the experiment. It was expected that the masks in the indoor groups that were left in the lab would release fewer microplastics than those left outside, and it was never expected that the indoor groups would release microplastics at a consistent rate throughout the entire experiment. As the masks were exposed to experimental conditions over longer periods of time, it would be expected that gradual embrittlement and weakening of the masks' tensile strength would result in an increase in microplastic release. Recent literature that has explored microplastic release in various PPE items. Morgana et al. (2021) has shown that time plays a strong role in the rate at which microplastics are released from various polypropylene-based materials. The R^2 obtained in this study supports this claim made in the aforementioned study and others.

It was, however, somewhat unexpected that the microplastic counts in the freshwater rinse groups would be higher initially and stabilize at a lower value over time. In the beginning of the study, it was expected that plastics released from the freshwater rinses would stay relatively consistent throughout the duration of the experiment. The most drastic changes occurred in the blue indoor freshwater rinses from week 1 to week 2, with a drop in nearly 1300 plastic particles and blue outdoor freshwater rinses from week 2 to week 3 with close to 1100 fewer plastics between weeks. It is currently unclear whether there is a correlation between microplastic release, light transmission and/or dry weight, but, for this experiment, the rate at which microplastics were released from the face masks does not explain variation in either of the other metrics. If biofilm or microbial accumulation played a role in the unexpected changes in light transmission and dry weight measurements, there is currently no indication that those factors could also affect microplastic release. More research will need to be conducted into evaluating the role of biofilms and microbes on each of the metrics used in this study.

Aside from ingestion of the entire face mask, microplastic release likely plays the most significant role in the marine-environmental plastic pollution problem. As shown in this study, a surgical face mask left in the marine environment for as little as a week can release anywhere from hundreds to thousands of microplastics, which can potentially affect marine life at all trophic levels (Marn et al. 2020). The longer an improperly disposed face mask or other PPE item remains in the ocean, the stronger the impact a single face mask can have on a given environment. It is difficult to determine what makes a plastic product fully "degraded" as macro-plastics degrade to microplastics, nano-plastics and beyond, and little is known about the rate at which different plastics degrade in seawater. To get a better understanding of this, multi-year or multi-decadal time scales studies are needed to accurately determine plastic degradation rates. In the interim, models of degradation, such as the one generated for this study are our best chance at addressing this question.

ATR-FTIR Spectroscopy – Carbonyl Index

The CI measured by the SAUB method in the inner and outer layers of all four mask types did not change over the course of the experiment. Acknowledging that the data was incomplete for this portion of the experiment, it was still expected that the CI in the inner and outer layers of each mask type would increase with time exposed to outside environmental

conditions. The inner and outer layers of blue indoor masks minimally changed, with a CI decrease in outdoor mask types. The SAUB method of calculating CI (Almond et al. 2020) is the most accurate method of determining the CI of all possible carbonyl species in polypropylene and polyethylene samples that have undergone photo-oxidation, compared to several other methods. However, there remains no standardized method for determining CI, and some methods work better for certain polymers than they do for others (Almond et al. 2020). For example, "method 5," which calculates CI by dividing the area of peaks at 1714 cm^{-1} and 1463 cm^{-1} is preferred for polypropylene samples, but is inconsistent for polyethylene (Almond et al. 2020, Table 3).

Inconsistencies with the CI data in this study could have been caused by the fact that surgical face masks are composed of several different polymers. Additives used in surgical face mask production may have also played a role in the CI values obtained in this study. The CI calculations from the SAUB method in the study by Almond et al. (2020) were derived from ATR-FTIR scans of pure polypropylene and polyethylene resins. This suggests that, if one were to try determining how degraded a sample from the environment is, the SAUB method or, even the CI in general, may not be an ideal metric to use. However, weathering and degradation, even under controlled situations, is not necessarily uniform across all samples. If this study had used the SAUB method to calculate the CI in the same samples from repeated measurements, perhaps the results would have been different. It is not unreasonable that the CI of blue indoor masks in this study essentially remained stable throughout the study due to the lack of exposure to sunlight, but it does not explain why the inner and outer layers of the black indoor masks exposed to the same conditions showed a statistically significant decrease in CI values.

Conclusion

This study was the first to measure rates of degradation in surgical face masks under these experimental conditions over a 16-week period. Of the metrics used in this study, microfiber counts from the seawater in the 2L bottles, and the freshwater rinses provided the best results. Based on the microfiber counts from the seawater and freshwater rinses, black masks kept outdoors and exposed to high temperatures and UV light degraded more than the other three types over the 16-week experiment. Black outdoor masks released 45% more microfibers than blue outdoor masks, and black masks in total released 49% more microfibers than both types of

blue masks. The logarithmic models generated for blue and black mask microfiber release show that microfiber release rate begins to plateau after approximately 100 years but does not reach a maximum, even after 500 years. The results overall indicate that no individual metric can solely be used to measure degradation, and that degradation does not happen uniformly across all samples. The bottle size and mask density within bottles may also have confounded the results. If this study were to be repeated, fewer masks would be placed in each bottle and repeated measurements of the same mask over time would have been used to assess degradation. Future studies on surgical mask degradation should also consider biofilm accumulation, as this likely had an impact on the results obtained from the dry weight and light transmission measurements. It is no secret that the COVID-19 pandemic had negative environmental repercussions, and more research needs to be done to accurately determine degradation rates of non-uniform plastic products and, perhaps, create and assign stages of degradation to plastics that are lost in the environment.

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