CSU The California State University
COUNCIL ON OCEAN AFFAIRS, SCIENCE & TECHNOLOGY (COAST)

Graduate Student Research Award Program
AY 2021-2022 Application Form
Application Deadline: Thursday, January 27, 2022, 5:00 p.m. PST

Please see information on Graduate Student Research Awards on the COAST **website** and read the **Announcement** for full details and instructions.

Save as both a Word document and a PDF file named as follows: *LastName_FirstName_App.docx* and *LastName_FirstName_App.pdf*. Submit both files as attachments, along with your **Advisor Sign-Off Form** and **Department Commitment Form** (if needed) in **ONE** email to graduate@share.calstate.edu. **Please note**: A signature is required from your advisor on the **Advisor Sign-Off Form** in the PDF version of your application that you submit (the word document does NOT need to be submitted with a signature). Your Advisor must submit your LOR to gradletter@share.calstate.edu separately.

Student Applicant Information

First Name:	Kelly	Last Name:	Hollman
CSU Campus:	San Diego State University	Student ID#:	
Email:		Phone:	
Degree Program:		Degree Sought (e.g., MS, PhD):	MS
Matriculation Date (mm/yy):		Anticipated graduation date (mm/yy):	
GPA in Major Courses:		Thesis-based? (Y/N):	Y

Advisor Information

First Name:	Natalie	Last Name:	Mladenov
CSU Campus:	San Diego State University	Department:	Civil, Construction, and Environmental Engineering
Email:		Phone:	

Research Project Title:	Photoirradiation and degradation kinetics of microfiber leachates
Project Keywords (5-7 keywords related to your project):	Microfibers, polyester, cotton, irradiation, leaching, degradation, kinetics

Budget Summary (must add up to $3,000)

Award amount directly to awardee:	3,000
Award amount to Department (DCF required for department funding):	0

The information on this page is for COAST use only and will not be shared with potential reviewers.

Have you previously received a COAST Graduate Student Research Award? (Y/N)	N
If yes, please provide year(s) of award(s):	

CSU Suggested Reviewers (Required): Suggested reviewers must be from the CSU. Use the COAST member database to help identify potential reviewers. Do not suggest any reviewers from your campus or reviewers with a potential conflict of interest.

Name:		
CSU Campus:		
Department:		
Email:		

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Please refer to the **Award Announcement** for detailed instructions on the information required for each of the following sections. All the boxes below will expand as you type.

Project Description (65 points total): 1,500-word maximum; any text over this limit will be redacted

Background

Microfibers (< 5 mm) are ubiquitous anthropogenic pollutants found in all major oceans (Barrows et al., 2018; Mishra et al., 2019). They can be synthetic (i.e., polyester, acrylic, nylon), natural/cellulose-based (i.e., cotton, wool, silk), semisynthetic (i.e., rayon), or blended (i.e. polyester/cotton) (Mishra et al., 2019). Synthetic microfibers, particularly polyester, have contributed significantly to microplastic pollution in marine environments due to the popularity of synthetic textiles and slow degradation rates (Mishra et al., 2019). In California, microfibers have been found in stormwater and treated wastewater, which are major sources of coastal microplastic pollution (Sutton et al., 2019). Most microfibers in urban stormwater runoff are from atmospheric deposition while microfibers are not completely removed by wastewater treatment plants (WWTPs) that receive them in washing machine effluents (Hartline et al., 2016; Murphy et al., 2016; Smyth et al., 2021; Talvitie et al., 2017).

Marine organisms are negatively impacted by ingesting microfibers in the water column (Mishra et al., 2019). Ingestion causes harmful effects such as gut damage, reduced food consumption, and exacerbation of preexisting health conditions among vulnerable species (Kim et al., 2021; Romanó de Orte et al., 2019, Watts et al., 2019). In fish guts collected from the Bay Area in California, microfibers comprised 87% of counted microparticles (Sutton et al., 2019).

Although there is now a more comprehensive understanding of the effects of microfiber particles on organisms and the environment, there is a major gap in our understanding of the chemicals that leach from microfibers in water. During textile processing, numerous chemicals are used, such as dyes, additives, and finishes. Many dyes, such as common azo dyes, are soluble organic compounds that do not easily degrade and are toxic to both aquatic organisms and humans (Berradi et al., 2019; Lellis et al., 2019). Additives and finishes, which may help prolong fabric lifespan, include different bisphenols (BPs) and benzophenone UV stabilizers, both of which are toxic (Sait et al., 2021; Xue et al., 2017).

Under UV irradiation during sunlight exposure, textile-related chemicals may persist or photodegrade (Sait et al., 2021; Sørensen et al, 2021). Leaching of these chemicals from microfibers may also be exacerbated by sunlight exposure compared to dark conditions (Kishor et al., 2021). Previous studies have quantified leaching and photodegradation of UV stabilizers from polyester, polyamide, and wool microfibers in seawater under UV irradiation (Sait et al., 2021; Sørensen et al, 2021). However, rate kinetics are unknown for a larger variety of textile-related chemicals that may also leach from other common types of fibers, including cotton and polyester/cotton. Desorption of dyes from cotton and polyester fabrics has been measured but not from microfibers (Cotton et al., 2020). While many dyes are light-resistant and may not degrade rapidly under sunlight, photochemical transformation/degradation rates of dyes that leach from microfibers are unknown (Kusic et al., 2006).

Research Objectives

To address gaps in our understanding of photochemical effects on both the leaching and degradation of dissolved chemicals derived from microfibers, I will build on the efforts of an existing project on assessing the fate and toxicity of microplastics under coastal environmental conditions. Synthetic (100% polyester), natural (100% cotton), and blended (50/50% polyester/cotton) microfibers will be leached in artificial seawater under realistic environmental conditions, including simulated sunlight or dark conditions, agitation, and varied size distribution of microfibers.

My research will delve further into the auto-fluorescent properties of leached compounds and develop new tools for tracking the leaching and degradation of dissolved constituents from microfibers. I will combine parallel factor analysis (PARAFAC) modeling of 3D fluorescence spectral matrix data of leached compounds with confirmation of fluorescent signatures of compounds identified from non-targeted analysis (obtained from the ongoing project). PARAFAC quantifies the contribution of dominant components in 3D-EEM spectra to total fluorescence, which is analogous to determining concentrations of fluorescent chemicals, or fluorophores (Wasswa et al., 2019). This approach will allow me to test the following hypotheses.

Hypotheses

I. *Similar DOC and TDN concentrations will be observed among leachates from different types of microfibers; however, differences in concentrations of dyes, additives, and finishes will result in different fluorescence signatures and intensities*. For example, since water-soluble reactive dyes are commonly used for natural fibers, leachates from cotton microfibers will have greater concentrations of dyes compared to polyester microfibers which are typically treated with insoluble dyes (Berradi et al., 2019).

II. *Sunlight exposure produces photo-oxidation reactions that will exacerbate leaching, particularly from polyester fibers, compared to leaching under dark conditions*. When compared to natural wool, synthetic fibers experienced surface degradation under UV irradiation, increasing available surface area for chemical leaching (Sørensen et al, 2021).

III. *After sunlight exposure, some parent chemicals persist while others will transform into degradation products*. For example, additives used for UV stabilizing are expected to degrade under sunlight (Sørensen et al, 2021). In contrast, commercial dyes are typically designed to resist light, and will not degrade readily under UV irradiation (Kusic et al., 2006).

Chemicals that leach may be fluorescent and quantified through fluorescence spectroscopy, a relatively rapid and nondestructive method that visualizes water contaminants as three-dimensional excitation-emission matrix (3D-EEM) spectra (Luo et al., 2019; Senesi & D'Orazio, 2005; Wasswa et al., 2019). 3D-EEM spectra will be acquired to determine leaching and transformation/degradation rates during sunlight and dark conditions. Fluorophores will be identified by comparing the 3D-EEM spectra of leachates to those collected from standards of various textile-related chemicals. In addition, since many textile-related chemicals are organic and have nitrogen groups, measuring dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations will provide valuable information about water quality after leaching.

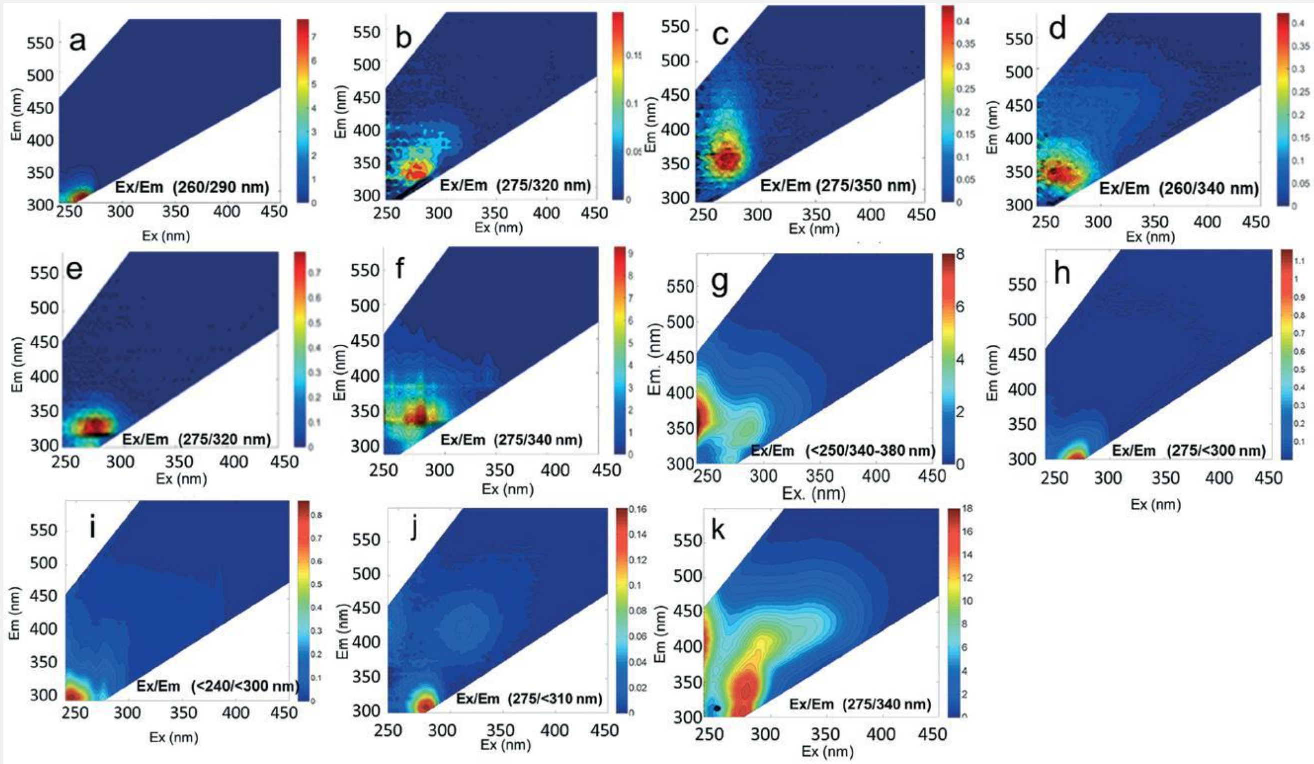

Figure 1. 3D-EEM spectra of various contaminants, such as g) oil from natural seep in seawater, (h) polyethylene plastic in water (Wasswa et al., 2019).

Methods

Experimental Design and Procedure

Microfibers will be produced from new, commercially available jersey t-shirts. All t-shirts will have the same color and are 100% polyester, 100% cotton, or 50/50% polyester/cotton. Fabric shavers (one per type of fiber) are used to produce microfibers in a negative pressure biosafety cabinet to reduce outside microfiber contamination. Microfiber size distribution is quantified using a Nikon Ti-2 epifluorescent microscope up to 100x magnification and a monochrome camera feature.

Batch leaching experiments will have a duration of 1 or 6 days with simultaneous sunlight-exposed and dark treatments. Two iterations of each experiment will be completed for replicability. Each treatment will have duplicate samples (10 g/L polyester, polyester/cotton, or cotton microfibers) and duplicate controls (artificial seawater only) in sterilized 400 mL wide-mouth beakers. A concentration of 10 g/L microfibers is used to produce higher concentrations of leachates that are more easily quantified (Sait et al., 2021). Each sample will have 3 g of a single type of microfiber. Both samples and controls will each have 300 mL of artificial seawater, which is sterilized and filtered. They will be continuously stirred using individual magnetic stirrers with 350 rotations/min to simulate laminar flow and mild agitation.

Among coastal WWTPs in California, those in the South Coast release the most treated effluent and consequently, large amounts of microfibers into the Pacific Ocean (Rodman et al., 2018). In sunlight-exposed treatments, a Suntest CPS+ Solar Simulator will be used to irradiate samples and controls with 470 W/m^2 total irradiation, including UV, to simulate average annual conditions in San Diego. Samples and controls will be irradiated with alternating 12 hours of exposure and 12 hours without exposure. In dark treatments, samples and controls will be placed inside aluminum foil-covered boxes to prevent light exposure.

Data Acquisition and Analysis

DOC and TDN concentrations will be measured at initial and final time points (1 or 6 days). Filtered 20 mL aliquots from each sample and control are analyzed using a Shimadzu TOC-L Total Organic Carbon and Total Nitrogen Analyzer with a high-temperature combustion method. Hypothesis I will be tested by evaluating DOC and TDN concentrations from leachates produced by different types of microfibers. When comparing more than two samples, analysis of variability (ANOVA) is performed to determine if there are statistically significant differences between concentrations.

3D-EEM spectra are acquired using a Horiba Aqualog Fluorometer with simultaneous UV-visible absorbance and fluorescence (from 200 nm - 550 nm emission) spectral acquisition. 3D-EEM spectra will be acquired at 30 min, 1 hr, 3 hr, 6 hr, 12 hr, and 24 hr for 1-day experiments. The same time points will be used for 6-day experiments in addition to 48 hr, 72 hr, 96 hr, 120 hr, and 144 hr. 4 mL aliquots from each sample and control are analyzed in sterilized cuvettes, then returned appropriately.

To further test hypothesis I, fluorophores identified by PARAFAC will be compared to spectral signatures of textile-related chemicals. Once identified, differences in concentrations of textile-related chemicals among different microfiber leachates may be determined. Changes in component contributions over time are used to calculate rate kinetics. Hypothesis II will be tested by comparing leaching rates to determine if sunlight exposure exacerbates leaching, especially from polyester. Hypothesis III will be tested by comparing photodegradation versus degradation rates in dark conditions to determine which fluorophores persist or degrade after sunlight exposure.

References (0 points): no limit

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Timeline (10 points total): 250-word maximum; any text over this limit will be redacted

Prior to COAST: August 2021 - May 2022	Conduct literature review of microfibers in the environment and their impact on marine ecosystems Conduct preliminary batch leaching experiments using new, undyed fabrics (100% polyester, 100% cotton, 50/50% polyester/cotton) while taking DOC/TDN and fluorescence spectroscopy measurements that will be compared to future results from new, dyed fabrics Produce significant quantities of microfibers from new, dyed jersey t-shirts (same compositions) for future experiments
May 2022 - August 2022	Conduct batch leaching experiments with simultaneous sunlight-exposed and dark treatments, two iterations of experiments for each type of microfiber, and duplicate samples and controls ● May 15 - end of month: 6-day and 1-day polyester iteration #1 ● June: 6-day and 1-day polyester iteration #2; 6-day and 1-day cotton iteration #1 ● July: 6-day and 1-day cotton iteration #2; 6-day and 1-day

	polyester/cotton iteration #1 ● August: 6-day and 1-day polyester/cotton iteration #2; begin writing thesis manuscript
September 2022 - December 2022	Conduct data analysis Continue with thesis Prepare paper about microfiber leachates for journal publication
January 2023 - May 2023	Continue with thesis Conference presentations
May 2023	Anticipated thesis defense

Need for Research (7 points total): 250-word maximum; any text over this limit will be redacted

While the ingestion of microfibers is known to harm marine organisms, the chemicals that leach from microfibers and their potential impacts are not well understood (Mishra et al., 2019). The proposed research will quantify DOC/TDN concentrations of microfiber leachates from different fabric compositions and evaluate fluorescent chemical leaching and transformation/degradation in realistic environmental conditions. Results will further inform policy change about managing microfiber pollution, for example, from domestic washing machines and municipal wastewater treatment, that ultimately impact marine environments. Implementing technology to filter microfibers from washing machine effluents, reducing microfiber loading in stormwater runoff, and improving capture in wastewater treatment is necessary for protecting oceans from known and unknown harms of microfibers.

Previous research has often focused on quantifying the number of microfibers released during domestic laundering or characterizing their distribution in environmental samples (Hartline et al., 2016; Napper & Thompson, 2016; Sutton et al., 2019). While there are trends in the number of microfibers released depending on fabric composition, it is unknown whether synthetic, natural or blended textiles are more likely to leach chemicals. Findings from this research will also support changes in textile processing and manufacturing that will consider the usage of more sustainable materials. For example, opting for textiles that are less likely to release microfibers and leachates will help reduce both microfiber pollution and further textile-related chemical loading in marine waters.

It may also be important to use biodegradable finishes, additives, and dyes when considering their potential to leach from microfibers.

Relevance to state of California (3 points total): 100-word maximum; any text over this limit will be redacted

The California Ocean Protection Council (OPC) is required to mitigate the ecological impacts of microplastics, such as synthetic microfibers, in coastal marine ecosystems (History of California Microplastics Legislation, 2020). The proposed research about the potential of microfiber leaching may aid the OPC in their efforts. Since it simulates conditions in California, it will support future state regulation of microplastics, especially in wastewater. In 2015, coastal WWTPs in California discharged 417.494 billion gallons into the Pacific Ocean which likely contributes significantly to microfiber pollution in marine environments (Hartline et al., 2016; Heal the Ocean, 2018; Murphy et al., 2016).

Budget and Justification (15 points total)

Example Budget (feel free to erase the content and use this format, adding additional rows as necessary, or create your own):

Item/Description	Unit Price	Quantity	Amount to Awardee (via Financial Aid)	Amount to Department
Rent	$675/month	4	$2700.00	
Gas	$0.575/mile (as per SDSU Mileage Rate for reimbursement)	26 miles/round trip to SDSU * 20 round trips	$300.00	
		Subtotals:	*$3000*	
		Grand Total	**$3,000.00**	

Justification (250-word maximum; any text over this limit will be redacted):

This award will cover the cost of rent for four months. This is largely helpful so that I can spend more time working on my research without taking an extra part-time job to help cover living expenses. Since I commute to campus, this award will also help pay for my gas expenses. I live approximately 13 miles from campus (26 miles round trip). Due to the nature of my research, I will often need to drive to campus every day (weekdays and weekends) to complete experiments. With 1 round trip/day, this award will also cover the cost of 20 round trips, which would help me accomplish two iterations of 6-day leaching experiments and at least one iteration of a 1-day leaching experiment.

- 6-day

1 day of setup and 12-hour sampling for fluorescence spectroscopy
+ 6 days of follow-up sampling for fluorescence spectroscopy and sample preparation for TOC analyzer
+ 1 day of data collection after TOC analysis
= 8 days or round trips * 2 = 16 days or round trips

- 1-day

1 day of setup and 12-hour sampling for fluorescence spectroscopy
+ 1 day of follow-up sampling for spectroscopy and sample preparation for TOC analyzer
+ 1 day of data collection after TOC analysis
= 3 days or 3 round trips

I would use this award during the 2022 Summer and Fall Semester when the majority of research experiments will be completed. It would be greatly appreciated in supporting my research and education.

Application Deadline: Thursday, January 27, 2022, 5:00 p.m. PST
Save as both a Word document and a PDF file named as follows:
***LastName_FirstName_App.docx* and *LastName_FirstName_App.pdf*.**
Submit both files as email attachments in ONE email (with other required forms) to graduate@share.calstate.edu.

Within 24 hours of application submission, you will receive a confirmation email from COAST. Please save this confirmation email for future reference. If you do not receive a confirmation email, please contact Kimberly Jassowski (kjassowski@csumb.edu) to ensure your application was received.

The California State University
COUNCIL ON OCEAN AFFAIRS, SCIENCE & TECHNOLOGY (COAST)

Graduate Student Research Award Program
AY 2021-2022 Advisor Sign-Off Form

To encourage you to engage with your CSU Advisor as you develop your application, **we are now requiring this Form for all applications submitted to the COAST Graduate Research Award Program**. By signing this form, your advisor indicates that they have reviewed your application, provided guidance and input, and approved it for submission. All information except signatures must be typed. Electronic signatures are acceptable. **Please note:** A signature is required from your advisor on this **Advisor Sign-Off Form** in the **PDF version** of your application that you submit (the word document does NOT need to be submitted with a signature)

Please note: this form is NOT a substitute for a letter of recommendation (LOR). Your Advisor must submit your LOR to gradletter@share.calstate.edu separately.

Applicant Name:

Kelly Hollman

CSU Advisor Information:

Name:	Natalie Mladenov	Phone:	(619) 594-0725
Department:	Civil, Construction, and Environmental Engineering	Email:	nmladenov@sdsu.edu

I have reviewed my student's application and provided guidance and input. My signature below indicates my approval of the application.

CSU Advisor Signature: ______________________ Date: January 27, 2022